Powder Diffraction & Rietveld Refinement

School

Durham University

8th April – 12th April 2018
Welcome to the Powder Diffraction & Rietveld Refinement School 2018!

The 4-day School will cover the fundamentals and practical aspects of powder diffraction and Rietveld refinement on data sets collected using a variety of different techniques and instrumentation. The course will begin with relatively straightforward examples of data analysis and build towards more complex refinements. For each topic there will be introductory formal teaching followed by practical problems. Expert tutors will be on hand to guide you with any difficulties! The aim is to understand the fundamentals of powder diffraction and Rietveld refinement rather than one specific software package. The structure of the afternoon practical sessions will be kept relatively flexible to allow you to work through problems at your own pace – don’t expect to finish them all.

The organisers would like to thank:

➢ The sponsors of the School:
  • The International Union for Crystallography (international student bursaries)
  • Durham University and Durham Chemistry Department (provision of facilities)
  • Bruker
➢ Alan Coelho and Bruker for providing Topas software for the School
➢ The tutors:
  • Josie Auckett
  • Matt Chambers
  • Huiyu Liu
  • Melissa Rodriguez-Garcia
  • Chloe Fuller
  • Luiza Rosa de Araujo
  • James Lewis

John Evans, Department of Chemistry, Durham University
Ivana Evans, Department of Chemistry, Durham University
Jeremy Cockcroft, Department of Chemistry, University College London
Andy Fitch, ESRF
Timetable and session plan

Lectures will be held in the Jimmy Knott hall at Trevelyan College except for Lecture 13 (Tuesday pm) and Lecture 23 (Thursday am) which will be in a chemistry lecture theatre. Please gather in the foyer of Collingwood College from ~15:15 on Sunday afternoon and we’ll walk to the teaching room together.

Afternoon practical sessions will be held in computer classrooms adjacent to the Chemistry department, CG66/68 (the “courtyard building”). Breakfast in college is 08.00 - 08.45. Morning lectures start at 9.00 sharp. All sessions are compulsory.

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<tr>
<td>09:00</td>
<td>3. Intro to (powder) diffraction</td>
<td>9. Structure factors, peak intensities &amp; Rietveld refinement</td>
<td>16. Peak shapes &amp; microstructure</td>
<td>23. Question &amp; answer/structure solution session</td>
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<td>11:00</td>
<td>Coffee</td>
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<td>11:30</td>
<td>5. Peak positions tutorial</td>
<td>11. Synchrotrons &amp; neutrons</td>
<td>18. Intro to GSAS/Fullprof</td>
<td>25. Free problems, GSAS, Fullprof then wrap up</td>
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<td>13:00</td>
<td>Lunch – Collingwood</td>
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<td>14:00</td>
<td>14.00 onwards Registration in Collingwood College</td>
<td>7. Least squares tutorial - excel</td>
<td>13. Interactive Rietveld refinement/Software intro</td>
<td>20. Rietveld problems - peak shapes</td>
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<tr>
<td>16:00</td>
<td>1. Symmetry</td>
<td>Tea</td>
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<tr>
<td>18:00</td>
<td>Dinner – Collingwood</td>
<td>Close</td>
<td>Dinner - Collingwood</td>
<td>19.00 Bar open</td>
</tr>
<tr>
<td>18:30</td>
<td>19.00 Symmetry tutorial</td>
<td>Dinner – Collingwood</td>
<td>“Fun” Tutorial</td>
<td>19.30 Course Dinner</td>
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<tr>
<td>19:30</td>
<td>19.00 Symmetry tutorial</td>
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<tr>
<td>20:00</td>
<td>Pub Quiz</td>
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Key: Lecture slot Other Practical
Tutorial Groups and Computer Accounts

For morning/evening tutorials you'll work in small groups of 8 students. Tutor groups will be allocated when you arrive. You should sit on the table allocated to your group. For hands-on computer practicals you'll need the Durham CIS login given to you at registration. Do not change the password!

<table>
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</table>
Computer classrooms CG66 and CG68 are marked above. You'll walk down the hill from Collingwood/Trevelyan Colleges and enter the Science Site by the fancy Physics building (P) near to point A on map above.
Collingwood College is 6. Jimmy Knott hall for lectures is at Trevelyan College (9). Collingwood to the Cathedral is ~15 minutes walk. CG66/68 and chemistry are near to 15. There’s a shop/bank at 27. The picture of the science area (12-14) is a bit out of date!
Software Used During the School

During the school we'll use the software packages below for analyzing and manipulating powder data and viewing structures. The j: drive is an area where you can store all your files. You have full write privileges in this area. The z: drive is a remote read-only drive where some of the software sits.

All school instructions are accessed via http://community.dur.ac.uk/john.evans/topas_workshop/pcg_workshop_menu.htm, which in turn can be found in your jEdit menus. Your jEdit menus will have links to various useful resources via the Help/General Links menu.

The software you'll need can be configured by running a command from the start menu. Hit start, navigate to “Rietveld” and select the Rietveld set up command. If you can’t find that, navigate to find z:\licence\rietveld\rietveld_setup.bat and run that file. Wait 5 minutes for installation to complete. Icons for jEdit and other software should appear on your desktop. You only need to run the setup procedure once.

Other packages are available from the z:\licence\rietveld\ drive.

Please work in a folder called j:\school_work or similar (there will be a shortcut to this on your desktop) and download data to that directory from http://community.dur.ac.uk/john.evans/topas_workshop/pcg_workshop_menu.htm. Do not save files in the j:\topas6 directory.

<table>
<thead>
<tr>
<th>Software</th>
<th>Description</th>
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<tbody>
<tr>
<td>Topas</td>
<td>Suite of programs for analysing powder and single crystal diffraction data.</td>
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<tr>
<td></td>
<td>Version 6 software has been kindly provided for the school by Bruker and Alan</td>
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<tr>
<td></td>
<td>Coelho. It’s licensed to Durham computers only.</td>
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<tr>
<td></td>
<td><a href="http://www.topas-academic.net/">http://www.topas-academic.net/</a></td>
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<tr>
<td>jEdit</td>
<td>Java editor that knows Topas syntax and is a rapid tool for creating input</td>
</tr>
<tr>
<td></td>
<td>files and interacting with Topas.</td>
</tr>
<tr>
<td></td>
<td><a href="http://community.dur.ac.uk/john.evans/topas_academic/jedit_main.htm">http://community.dur.ac.uk/john.evans/topas_academic/jedit_main.htm</a></td>
</tr>
<tr>
<td>Expgui</td>
<td>A graphical front end provided by Brian Toby to run Bob Von Dreele/Alan</td>
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<tr>
<td></td>
<td>Larson’s GSAS software package for analyzing diffraction data.</td>
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<tr>
<td>PC-gsas</td>
<td>A less user friendly but more powerful front end to gsas provided by Bob</td>
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<tr>
<td></td>
<td>Von Dreele.</td>
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<tr>
<td>GSAS-II</td>
<td>The latest developmental version of GSAS. For the brave?</td>
</tr>
<tr>
<td>Fullprof</td>
<td>Suite of programs written by Juan Rodriguez-Carvajal.</td>
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<td><a href="http://www-llb.cea.fr/fullweb/fp2k/fp2k_intro_ref.htm">http://www-llb.cea.fr/fullweb/fp2k/fp2k_intro_ref.htm</a></td>
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<tr>
<td>Mercury</td>
<td>A structure viewer written by Cambridge Crystallographic Data Centre.</td>
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<td>Excel</td>
<td>Spreadsheet</td>
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<tr>
<td>xch</td>
<td>Useful for converting Bruker data format files to ascii</td>
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<tr>
<td>xytogsas/v6xytogsas</td>
<td>Convert xy files to gsas format</td>
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<tr>
<td>xyconv</td>
<td>Manipulate an xy file</td>
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Selected References

The list below contains some references that you might be interested in looking at after the course.

Books – see references 1-7.
Webpages – see references 8-14.
Papers – see references 15-25.
Software mentioned in the course – see references 13, 26-28.

This is to certify that:

..................................................................................

attended the **Powder Diffraction & Rietveld Refinement School 2018**

at Durham University, 8\(^{th}\) April – 12\(^{th}\) April 2018.

Signed:

..................................................................................

Prof John S.O. Evans
Professor of Solid State Chemistry
Durham Chemistry
This is to certify receipt of payment of

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from

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for costs associated with the Powder Diffraction & Rietveld Refinement School 2018 at Durham University, 8\textsuperscript{th} April – 12\textsuperscript{th} April 2018.

Signed:

..............................................................................................................

Dr Ivana Evans
Senior Lecturer in Structural/Materials Chemistry
Durham Chemistry
## Pre-Course Questionnaire

If you’d like the questionnaire to be anonymous use a pseudonym instead of your name, but please use the same pseudonym in the post-course questionnaire!

<table>
<thead>
<tr>
<th>Name or pseudonym:</th>
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<tbody>
<tr>
<td>University (optional):</td>
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<tr>
<td>Department (optional):</td>
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<tr>
<td>Research area (e.g. thesis title):</td>
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<tr>
<td>Years of research:</td>
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<tr>
<td>Approximately how many structures have you refined by the Rietveld method? Were they molecular or extended structures?</td>
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<tr>
<td>List data types you have worked with (e.g. lab X-ray, tof neutron, etc):</td>
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<tr>
<td>List Rietveld software used:</td>
</tr>
<tr>
<td>State crystallographic training/knowledge (e.g. one undergraduate course a long time ago; practising single crystal person; etc)</td>
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<tr>
<td>Are there specific areas you’re hoping will be covered in the course?</td>
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# Post-Course Questionnaire

Please tick boxes as relevant and add any additional text comments you fancy.

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<th>Name/pseudonym:</th>
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1. Was the balance of theory and practical exercises:  
   
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<th>Good</th>
<th>4</th>
<th>3</th>
<th>2</th>
<th>1</th>
<th>0</th>
<th>Bad</th>
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   Comments:  
   

2. How useful did you find the tutorial group problem sessions:  
   
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<th>Useful</th>
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<th>2</th>
<th>1</th>
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<th>Useless</th>
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   Comments:  
   

3. How useful did you find the computer based problem sessions:  
   
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   Comments:  
   

4. How difficult did you find the problems:  
   
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<th>Easy</th>
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   Comments:  
   

5. Overall satisfaction with the teaching school:  
   
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<th>Happy</th>
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<th>2</th>
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<th>Sad</th>
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</table>
   
   Additional comments on the academic aspects of the school:  
   

Any comments on the non-academic aspects of the school:  


Classroom Tutorial Problems

Session 2: Symmetry

1. The wallpaper figures below illustrate some aspects of 2-dimensional symmetry.
    a. Identify the symmetry elements present.
    b. Draw the most appropriate unit cell on the figure.
    c. State the plane group symbol (a plane group is the 2-dimensional equivalent of a space group).

2. The diagram below shows a primitive space group with the position of a molecule marked with a shaded circle (O*). Some other positions in the unit cell have been labelled A to S so we can refer to them (N.B. these © type symbols don’t represent molecules, just positions in the cell):
   a. Which crystal system does this space group belong to?
   b. Suggest a space group symbol.
c. Which of the labeled positions A to S correspond to the symmetry equivalent positions of our original molecule (O⁺) within the unit cell?

d. Label the heights of each of the symmetry-generated molecules within the unit cell.

3. Using the information given in the extracts from the publication below:
   a. State which atoms are on special/general positions
   b. State the Wyckoff site and site symmetry for each
   c. Work out the formula from the crystallographic data
   d. Consider possible reduction of the compound. Deduce the formula if:
      i. Site O1 is only 75% occupied
      ii. Site O2 is only 25% occupied
Synthesis and Structure of BiCa$_2$VO$_6$

I. Radosavljevic, J. S. O. Evans, and A. W. Sleight$^1$

Department of Chemistry and Center for Advanced Materials Research, Oregon State University, Corvallis, Oregon 97331-4003

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A new compound, BiCa$_2$VO$_6$, has been synthesized and its structure determined. This compound crystallizes in space group Cmc$2_1$ (No. 36) with $a = 8.892$ Å, $b = 11.961$ Å, $c = 5.546$ Å, and $Z = 4$. Both high-resolution X-ray and neutron powder diffraction data were used in the refinement of the BiCa$_2$VO$_6$ structure. This structure can be described as composed of (BiO$_2$)$_2$ chains, VO$_4^2-$ tetrahedra, and Ca$^{2+}$ cations leading to a BiO$_2$Ca$_2$VO$_6$ structural formula. This compound is potentially ferroelectric where switching polarity would mainly involve rotations of VO$_4$ tetrahedra.

INTRODUCTION

Crystallographic Details:

<table>
<thead>
<tr>
<th>Atom</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>Occ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi1</td>
<td>0</td>
<td>0.0894(6)</td>
<td>0.250(0)</td>
<td>1</td>
</tr>
<tr>
<td>Ca1</td>
<td>0.2999(4)</td>
<td>0.3927(3)</td>
<td>0.242(1)</td>
<td>1</td>
</tr>
<tr>
<td>V1</td>
<td>0</td>
<td>0.161(2)</td>
<td>0.199(4)</td>
<td>1</td>
</tr>
<tr>
<td>O1</td>
<td>0.3492(4)</td>
<td>0.9970(3)</td>
<td>0.492(1)</td>
<td>1</td>
</tr>
<tr>
<td>O2</td>
<td>0</td>
<td>0.8168(3)</td>
<td>0.005(1)</td>
<td>1</td>
</tr>
<tr>
<td>O3</td>
<td>0</td>
<td>0.9481(4)</td>
<td>0.568(1)</td>
<td>1</td>
</tr>
<tr>
<td>O4</td>
<td>0.1548(4)</td>
<td>0.2472(3)</td>
<td>0.079(1)</td>
<td>1</td>
</tr>
</tbody>
</table>

4. A powder pattern is indexed as orthorhombic and the following reflections are definitely observed: 200, 121, 022, 110, and 312. Which Bravais lattice type best matches these observations?
5. The peaks in a PXRD pattern may be indexed as orthorhombic with hkl indices assigned to the first 20 peaks as given in the table below. Which of the following space groups is the most likely one for the structure of this compound: Cmca, P2₁2₁2₁, Pnma, Fddd, or Pbca?

<table>
<thead>
<tr>
<th>2θ (°)</th>
<th>d (Å)</th>
<th>h</th>
<th>k</th>
<th>l</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.015</td>
<td>7.1547</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>9.458</td>
<td>6.0650</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>10.111</td>
<td>5.6743</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>11.468</td>
<td>5.0047</td>
<td>1</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>12.013</td>
<td>4.7783</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>12.961</td>
<td>4.4300</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>13.803</td>
<td>4.1612</td>
<td>2</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>14.555</td>
<td>3.9471</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>15.625</td>
<td>3.6784</td>
<td>1</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>15.764</td>
<td>3.6462</td>
<td>2</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>2θ (°)</th>
<th>d (Å)</th>
<th>h</th>
<th>k</th>
<th>l</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.069</td>
<td>3.5773</td>
<td>2</td>
<td>0</td>
<td>2</td>
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<tr>
<td>16.465</td>
<td>3.4918</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>16.807</td>
<td>3.4213</td>
<td>0</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>17.922</td>
<td>3.2100</td>
<td>0</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>18.026</td>
<td>3.1916</td>
<td>1</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>18.414</td>
<td>3.1249</td>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>18.981</td>
<td>3.0325</td>
<td>0</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>19.276</td>
<td>2.9864</td>
<td>2</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>19.660</td>
<td>2.9287</td>
<td>1</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>20.070</td>
<td>2.8695</td>
<td>3</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

6. A heavy atom hydride undergoes a phase transition giving a power diffraction pattern that may be indexed in terms of a nearly cubic unit cell where a ≈ b ≈ c and α ≈ β ≈ γ ≈ 90°. The structure for the layers z ≈ 0 (solid) and z ≈ 1/4 (open) is shown below. The layers at z = 1/2 and z = 3/4 are similar to the previous ones, being generated by a shift of 0,1/2,1/2. What symmetry elements are present and what is the space group?
Session 3/4/5: Intro to Diffraction and Peak Positions Tutorial

1. Write the Miller indices for planes which form the intercepts with the crystallographic axes given below. You might find it easiest to draw simple sketches of each plane.
   a. a, -b/2, ||c;
   b. 2a, b/2, c/2;
   c. ||a, ||b, -c;
   d. a, -b, 3c/4;
   e. ||a, -b/4, c/3;
   f. -a/4, b/2, -c/3.

2. Determine and list in order of increasing angle the values of 2θ and the indices for the first three reflections in powder patterns recorded using Cu Kα radiation on materials with lattices below. For a tetragonal material d-spacings are given by $1/d^2 = (h^2+k^2)/a^2 + l^2/c^2$.
   a. primitive tetragonal, $a = 2.00$ Å, $c = 3.00$ Å
   b. primitive tetragonal, $a = 3.00$ Å, $c = 2.00$ Å

3. Figure 1 shows powder diffraction patterns of two cubic materials recorded with $\lambda = 1.54$ Å. Index each and comment on their symmetry. Comment on any reflections you cannot index.

4. Figure 2 is a powder pattern of tetragonal rutile for which $a \approx 4.5$, $c \approx 2.96$ Å. Try to index this pattern. You can explore this example further using an excel spreadsheet to help index then refine the cell during the computer tutorials.
Figure 1 Diffraction data recorded with $\lambda = 1.54$ Å for two cubic materials
Figure 2: Diffraction pattern of TiO$_2$

Session 6: Least Squares

1. Find the best fit line that passes through the points (1,2), (3,5), (6,10). Calculate the standard uncertainty and correlation coefficient between gradient and intercept. Comment on the sign of the correlation coefficient.

2. Add a restraint that the line should pass through the origin. How do the values of gradient and intercept change?
Session 9: Structure Factors and Peak Intensities

1. As part of an undergraduate practical class a student was asked to record powder diffraction patterns of the compounds BaS and SrSe, both of which have the rock salt structure (as shown below). Ionic radii (Å) are Ba 1.49, Sr 1.32, S 1.70, Se 1.84. Unfortunately the student forgot to label the patterns (which are shown in figure 3). Can you help identify which is which?

2. Show that for the NaCl structure the conditions for observing reflections in a powder pattern are:
   
   \[ \text{h,k,l all even, } F_{hkl} = 4(f^* + f) \]
   
   \[ \text{h,k,l all odd, } F_{hkl} = 4(f^* - f) \]
1odd, 2 even or 2 even, 1 odd, $F_{hkl}=0$

Note that the structure factors can be calculated by considering whole atoms in one octant of the unit cell.

3. TiO$_2$ in the rutile form has $a = 4.59$, $c = 2.96$ Å. Ti is at (0,0,0) and O close to (0.3,0.3,0). The intensity of a reflection in the powder pattern is given by:

$$I_{hkl} = F_{hkl}^2 \times LP \times mult \times scale$$

The structure factor is given by:

$$F_{hkl} = f_T A_T + f_O A_O$$

For Ti the contribution is:

$$A = 2 \cos^2 \pi \left( \frac{h+k+l}{4} \right)$$

For O the contribution is:

$$A = 2 \cos 2\pi \left[ \cos 2\pi \left( \frac{hx-h+k+l}{4} \right) \cos 2\pi \left( \frac{ky+h+k+l}{4} \right) \cos 2\pi \left( \frac{kx-h+k+l}{4} \right) \cos 2\pi \left( \frac{hy+h+k+l}{4} \right) \right]$$

The Lorentz-Polarisation factor for a lab diffractometer with $2\theta_{mono}=26.6$ is:

$$LP = \frac{1 + \cos^2 \left( 2\theta_{mono} \right) \cos^2 \left( 2\theta \right)}{\sin^2 \theta \cos \theta}$$

For the (020) reflection calculate:

a. The $2\theta$ value;

b. The LP factor at this $2\theta$ value;

c. The structure factor ($f_T=15.43$, $f_O=5.28$ at 39.2º $2\theta$);

d. The intensity of the reflection assuming a scale factor of 0.0069.

Note that this problem is closely related to the excel Rietveld refinement problem.

**Session 10: Data Collection**

1. You have been provided with a data file containing columns of $2\theta$ and intensity collected on a laboratory instrument using variable slits. Before attempting a Rietveld refinement what correction should you apply to the data? What should you do about standard uncertainties? What would be the symptom of not applying any corrections in a Rietveld refinement?

2. One of the basic assumptions in Rietveld refinement of Bragg-Brentano data collected with a divergent beam is that the sample is infinitely thick so that the effective irradiated volume is independent of $\theta$ (at low $\theta$ you have a large area illuminated but the effective beam penetration depth is small; at high $\theta$ you have a smaller area but a larger penetration depth). Assuming that the intensity diffracted by a layer at depth $x$ is given by the equation below, estimate how thick a powdered Ni metal sample must be to be "infinitely thick". You may assume that when the intensity diffracted by a layer of the sample is 1/1000th that of the top surface its contribution is negligible.
\[ I_x \propto \frac{I_0}{\sin \theta} \exp(-2\mu x / \sin \theta) \]

Information: density Ni 8.9 g/cm\(^3\); packing density of Ni powder 60%; Cu K\(\alpha\) radiation; assume \(\theta = 90^\circ\); mass absorption coefficient of Ni 48.83 cm\(^2\)/g for Cu K\(\alpha\).

Repeat the calculation for an organic material assuming a density of 1 g/cm\(^3\) and a mass absorption coefficient of 4.2 cm\(^2\)/g.

Comment on your answers.

3. What capillary size would you use to measure samples of Bi\(_2\)O\(_3\) and Fe\(_2\)O\(_3\), using X-rays of wavelength (a) 0.410 Å, (b) 0.825 Å?

Information: Bi\(_2\)O\(_3\) density 8.9 g/cm\(^3\); Fe\(_2\)O\(_3\) density 5.2 g/cm\(^3\); all powder packing densities 60%; atomic masses: Bi 208.98, Fe 55.85, O 15.9994; mass absorption coefficients for \(\lambda = 0.41\) Å: Bi 31.520 cm\(^2\)/g, Fe 8.176 cm\(^2\)/g, O 0.378 cm\(^2\)/g; mass absorption coefficients for \(\lambda = 0.825\) Å: Bi 156.000 cm\(^2\)/g, Fe 67.080 cm\(^2\)/g, O 1.836 cm\(^2\)/g.

Session 11: Synchrotrons and Neutrons

1. Assuming a powder X-ray diffractometer’s mechanical upper 2\(\theta\) limit to be 140\(^\circ\), estimate the smallest d-spacing accessible using a laboratory machine running with Cu K\(\alpha1\) radiation (\(\lambda \approx 1.5406\) Å), and a synchrotron diffractometer running with an X-ray photon energy of 31 keV.

2. Titanium has a hexagonal close packed structure with cell parameters a = 2.95 Å and c = 4.686 Å. Calculate the expected 2\(\theta\) position for the 400 reflection (d = 2.95 \times \sin(120) / 4 = 0.639 Å) for the synchrotron and the lab machines in question 1.

3. Silica (SiO\(_2\)) glass (sometimes called “quartz glass”) can be a convenient material from which to construct reaction cells for the in-situ investigation of chemical processes by powder diffraction. Estimate the proportion of the radiation absorbed by a silica-glass cell with wall thicknesses of 1 mm for neutrons of wavelength 1.8 Å (absorption coefficient \(\mu = 3.8 \times 10^{-4} \text{ mm}^{-1}\)), Cu K\(\alpha\) (\(\mu = 7.58 \text{ mm}^{-1}\)) and 31 keV photons from the synchrotron (\(\mu = 0.12 \text{ mm}^{-1}\)), given the normal Beer-Lambert law for absorption \(I = I_0 \exp(-\mu l)\), where \(l\) is the path length in the absorbing material. Repeat the calculation for Cu radiation and a thin-walled silica-glass capillary, commonly supplied for high-temperature X-ray diffraction, with a wall thickness of 10 \(\mu\)m.

4. The UK’s Diamond synchrotron radiation source runs at 3 GeV and has a circumference 561.6 m (24 sectors). How many electrons are there in the ring when the machine is operating at its design current of 300 mA?

(Electronic charge \(= 1.602 \times 10^{-19}\) C, speed of light \(= 299792458\) m s\(^{-1}\), a current of 1 A is a flow of charge of 1 C s\(^{-1}\).
5. Discussion: A sample that was used to characterise the intrinsic resolution and peak shape of a powder diffractometer is the NIST (National Institute of Standards and Technology) standard 660a, LaB$_6$. This is a highly crystalline material that has very few defects and hence intrinsically narrow diffraction line widths. Would this be a suitable standard for:
   a. flat-plate laboratory machine using Cu K$\alpha$ radiation ($\mu \approx 110$ mm$^{-1}$ if 100% packing density)?
   b. laboratory capillary diffractometer (Cu K$\alpha$)?
   c. 31 keV synchrotron machine ($\mu \approx 2.8$ mm$^{-1}$, 100% packing density)?
   d. powder neutron diffractometer ($\mu \approx 6.4$ mm$^{-1}$ due to 20% $^{10}$B in natural B)?

6. Discussion: To help to characterise the distribution of Co and Fe disordered over two crystallographic sites in a structure, what powder diffraction techniques could you use?

7. For a time-of-flight (tof) diffractometer such as HRPD at ISIS, d-spacing and tof are related by the expression $\text{tof} = \text{difa} \times d^2 + \text{difc} \times d + t0$. difc is related to the instrument flight path, difa and t0 are corrections (usually minor). The figures below show the pattern of a cubic material with $a = 9.18$ Å collected on the backscattering 168 degree (top) and 90 degree (bottom) detector banks. Instrument constants are:
   (t0_hrp_d_90, 25, difc_hrp_d_90, 34732, difa_hrp_d_90, -2.0)
   (t0_hrp_d_bs, -8.8, difc_hrp_d_bs, 48291, difa_hrp_d_bs, -4.6)
   (a) Calculate the approximate d-spacing ranges for each of the detector banks (Hint: you can ignore difa and t0 terms).
   (b) Calculate the tof you would expect for the (422) reflection in each data set.
   (c) Sketch on your copy of the figure the relationship between peaks in the back scattering and 90 degree banks.
   (d) What are the pros and cons of the back scattering and 90 degree banks?
Session 16: Peak Shapes and Microstructure

1. Use the Scherrer formula \( \text{fwhm} = K \frac{\lambda}{\text{size} \cdot \cos \theta} \) (\( K = 0.9 \)), where fwhm is measured in radians, to obtain a crude estimate of the size of the crystalline domains in Figure 5 (a) and (b) which were recorded with \( \lambda = 1.54 \) Å.
Session 17: Restraints and Constraints

1. Try the problem from Session 6 on linear regression and add a restraint that the straight line should pass through the origin. Investigate the influence of different weightings on the restraint.

2. Discussion: You're trying to determine the structure of $\text{WO}_3$ from powder diffraction data. How would you get the most reliable structure possible?
Computer tutorials

Tutorial Problems

All the tutorials are on the web at:
http://community.dur.ac.uk/john.evans/topas_workshop/pcg_workshop_menu.htm

All the data files are linked from the tutorials or can be found at:
http://community.dur.ac.uk/john.evans/topas_workshop/data/

This site can be accessed directly from the jedit Help/General/Links menu. It should also be in your explorer favourites.

All the tutorials below will be available during the school. They may be renumbered relative to this list.

Session 7/8 - Least Squares Refinement - Excel

These tutorials are intended to introduce you to least squares refinement. We'll use the solver function of excel to perform various least squares fits. We'll start fitting a straight line then move on to fitting Gaussians and eventually performing a full Rietveld refinement. We'll use topas to perform equivalent refinements to those in excel.

Tutorial 1 - Fitting straight lines, quadratics and Gaussians in excel.
Tutorial 2 - How to perform the same fits from Tutorial 1 in Topas.
Tutorial 3 - How to refine unit cell parameters in excel.
Tutorial 4 - How to perform Pawley and Rietveld refinements in excel.
Tutorial 5 - Indexing: How to index a tetragonal powder pattern and refine unit cell parameters using excel.

Session 8 - Peak Positions/Indexing

Peak positions are one of the fundamental aspects of a diffraction pattern and are determined by the cell size and shape. These tutorials look at how unknown unit cells are obtained/refined. You can try these procedures on any of the other data sets provided. If you've never used topas/jedit before you might want to try e.g. tutorial 8 or tutorial 9 first which go through some of the mechanics of using jedit in a bit more detail.

Tutorial 6 - Peak Fitting: How to perform individual peak fitting in topas, often the first step before indexing.
Tutorial 7 - Indexing: How to index a powder pattern in topas.

Session 14 - TA/Simple Rietveld refinement in jedit/Topas

The tutorials below are intended to give you an introduction to Rietveld and Pawley refinement using the topas/jedit interface. The aim of the tutorial session is not to necessarily fully understand what your doing, but to make sure you're happy with the "mechanics" of the overall process of Rietveld refinement.
If you want even more basic tutorials on topas/jedit then take a look at the introductory tutorials on the web. The examples there have far more detail and contain screen shots of (approximately) what you should see at each stage.

**Tutorial 8** - How to run a prewritten input file.

**Tutorial 9** - TiO2 Rietveld: A simple Rietveld refinement of lab data.


**Tutorial 11** - Pawley Fitting: Pawley fitting is a structure independent whole pattern fitting method. It’s a good way of finding if a unit cell is correct and also finding the "best possible" fit you’d get by Rietveld.

**Tutorial 12** - ZrW2O8 Rietveld: Simple Rietveld refinements of lab data, constant wavelength neutron and time of flight neutron data - make sure you have john's `local.inc` on your computer.

**Tutorial 13** - Multiphase Rietveld refinement

**Tutorial 13.5** – LaMnO3 with no detailed instructions.

**Session 15 - Neutron/Synchrotron/Combined Refinement**

How to perform Rietveld/Pawley refinements using neutron/synchrotron data. As well as these examples you might want to repeat/complete the exercises from session 13.

**Tutorial 14** - Y2O3 data recorded on id31 at the esrf

**Tutorial 15** - ZrW2O8 Rietveld: Simple Rietveld refinements of lab data, constant wavelength neutron and time of flight neutron data - make sure you have john's `local.inc` on your computer.

**Tutorial 16** - PbSO4 neutron data Jeremy discussed are here.

**Tutorial 17** - Combined Refinement: Builds from earlier tutorial on ZrW2O8 and shows how to simultaneously fit X-ray and neutron data. Also discusses structure solution from X-ray and neutron data. See also gfas 3 and gfas 4.

**Session 20 - Peak Shapes**

Peak shapes are another fundamental aspect of a diffraction pattern. These tutorials investigate some of the functions used in Rietveld packages and how peak shapes can be used to give size/strain information.

**Tutorial 18** - This tutorial explores convolutions to fit a single peak in a pattern as discussed in lectures.

**Tutorial 19** - In this tutorial you'll investigate the various peak shape functions that are used in Rietveld refinement packages. You'll use experimental fwhm vs 2-theta data in excel to come up with functions that might describe a real data set. You'll then try these functions in topas.

**Tutorial 20** - Fundamental Parameters peak shape fitting.

**Tutorial 21** - Size/Strain Analysis: Shows how size/strain can be determined in topas using the CeO2 round robin data.

**Tutorial 22** - Nanoparticle Sizing: Determines the size of ~2 nm particles from diffraction data.
Session 21 - Restraints/Rigid Bodies
Use of extra chemical information such as restraints and rigid bodies is often important when analysing powder data. Several of the tutorials (e.g. the one on ZrW2O8 Rietveld) use bond distance and angle restraints. Tutorials in this section provide more examples.

Tutorial 23 - Rietveld refinement of an organic molecule using restraints and rigid bodies. See also gsas 7.

Tutorial 24 - A complex use of rigid bodies to refine 3 molecules in asymmetric unit with z-matrix description of local bodies to constrain internal symmetry. Data recorded on id31.

Session 22 - Neutron and X-ray Combined Refinement
How to perform a combined refinement using neutron and X-ray data.

Tutorial 17 - Combined Refinement: Builds from earlier tutorial on ZrW2O8 and shows how to simultaneously fit X-ray and neutron data. Also discusses structure solution from X-ray and neutron data. See also gsas 3 and gsas 4.

Session 21/22/25 - GSAS/Fullprof Examples
These examples are similar to those you have/will perform in the topas tutorials and are designed to give you a feel for other widely used (and free) Rietveld packages. It's very important to use a range of software as different packages have different strengths. GSAS and Fullprof, for example, handle magnetic refinements which currently can't be done in topas. The packages come with many of their own built-in tutorials. The examples below deliberately repeat the analyses done in topas.

GSAS 1 - Y2O3 laboratory data
GSAS 2 - PbSO4 neutron data
GSAS 3 - ZrW2O8 neutron data
GSAS 4 - ZrW2O8 restraints and combined refinement
GSAS 5 - Sc2(WO4)3 rigid bodies
GSAS 6 - CFBr3 organic
GSAS 7 - A medium sized organic using restraints
GSAS 8 - NiL2 coordination compound with restraints
GSAS 9 - Quantitative Rietveld

Fullprof 1 - Y2O3 lab data in fullprof

Session 24 - Spot the Errors
These tutorials are designed to teach you how to trouble-shoot Rietveld refinements.

Tutorial 25 - Trouble shooting.

Session 25 - Structure Solution
Structure solution is not formally part of the course, but you could try the tutorials below if you're interested. The tutorial on combined refinement of ZrW2O8 also explores these ideas.

Tutorial 26 - Structure Solution of an inorganic oxide: Takes the information from earlier tutorials and solves the structure of TiO2 using simulated annealing.

Tutorial 27 - Structure solution of a rigid organic molecule and other examples.
Tutorial 28 - Structure solution of inorganic materials.

Session 25 - Miscellaneous Examples
C:\webpages\topas_workshop\tutorial_ceo2_sizestrain.htm - Quantitative Rietveld refinement. This is extremely important in many industries. This example uses the Round Robin data of Ian Madsen and Nikki Scarlett.
C:\webpages\topas_workshop\tutorial_nano_size.htm - Size/Strain Analysis: Shows how size/strain can be determined in topas using the CeO2 round robin data.
C:\webpages\topas_workshop\tutorial_nano_size.htm - Nanoparticle Sizing: Determines the size of ~2 nm particles from diffraction data.
Tutorial 30 - Solving a structure from single crystal data using charge flipping
Tutorial 31 - Single crystal: How to do a simple single crystal refinement in topas.

Session 25 - Parametric/Surface Refinement
Tutorial 34 - Parametric or surface Rietveld refinement - how to use surface fitting to analyse 100 patterns simultaneously to follow phase transitions in WO3.
Tutorial 35 - Parametric or surface Rietveld refinement - how to refine temperature using the ZrP2O7 example.

Session 25 - Symmetry Mode Refinements
Tutorial 36 - Structural transformations. Directly refine symmetry-mode amplitudes rather than traditional atomic xyz coordinates of a distorted superstructure. Example based on simulated lab x-ray diffraction data from low-temperature orthorhombic LaMnO3. The symmetry modes are obtained using the ISODISTORT software.
Tutorial 37 - Structural transformations. Directly refine symmetry-mode amplitudes rather than traditional atomic xyz coordinates of a distorted superstructure. Example based on laboratory x-ray diffraction data from room-temperature monoclinic WO3. The symmetry modes are obtained using the ISODISTORT software.
Tutorial 38 - Structural transformations. A more advanced symmetry-mode refinement example based on room-temperature WO3. Fit both neutron and X-ray data. Try to determine space-group symmetry at high temperature using ISODISTORT.
Tutorial 41 - By combining topas, ISODISTORT and some python scripts you can automatically search through different space group possibilities for samples which undergo symmetry-lowering phase transitions.

Session 25 - Magnetic Refinements
Tutorial 39 - Topas v5 will perform magnetic Rietveld refinement. This tutorial takes you through three different ways of describing the low temperature magnetic structure of LaMnO3.
Session 25 - Stacking Fault Refinements

Tutorial 40 - Topas v6 lets you calculate the diffraction of materials with stacking faults. This tutorial takes you through this type of analysis using examples from the DIFFaX software package.
Session 0: Welcome/Introduction

Prof John S.O. Evans
Durham University

Teachers/Tutors

- Jeremy Cockcroft UCL
- John Evans Durham Chemistry
- Ivana Evans Durham Chemistry
- Andy Fitch ESRF
- Josie Auckett
- Matt Chambers
- Huiyu Liu
- Melissa Rodriguez-Garcia
- Chloe Fuller
- Luiza Rosa de Araujo
- James Lewis

Thanks

- Tutors/lecturers for time
- Sponsors for cash
- Alan Coelho/Brucker for Topas software
- Bob von Dreele/Brian Toby for gsa
- Juan Rodriguez-Carvajal for fullprof

Welcome

- Health and Safety/Fire procedures
- Course will be lectures, small group tutorials and hands-on computer practicals
- Please submit pre-course questionnaire with name/pseudonym
- Tell us during school if there are things you’d like covered
Legalities

• By using ITS account you’re agreeing to University policy on use of the web

• You each have your own login id. Don’t change the password!!!

• Don’t try stealing the software! It won’t work anywhere else.

• Topas controlled by license server “codemeter” which should be installed on your CIS computer

• All timetabled sessions are compulsory
• Always wear a name badge
• No email during lectures/classes (teachers behind you!)

House Keeping/Arrangements

• Morning sessions will be lectures/small group tutorials in Jimmy Knott Hall
• Afternoon sessions will be in computer classrooms near Chemistry
• All lunches/dinner in college
• Evening events in bar or tbc

What the course isn’t meant to be…..

• How to use topas
• How to use gsas
• How to use fullprof

• How to perform magnetic refinements (though some tutorials)

• Linear/complete in its organisation
  – 3 days of theory lectures + 1 day hands-on = bad
  – Sometimes you’ll be doing problems “blind” – trust us!
  – There are more problems in booklet than time available
  – Some practicals will come before the relevant theory
  – You’ll learn by mistakes
  – Confusion can be good

The course is meant to…..

• Provide understanding of what to think about when collecting (powder) diffraction data
• Provide understanding of what Rietveld packages are doing
• Allow you to practice Rietveld refinement
  – Different instruments
  – Different samples
  – Different problems
• Teach you to be critical/creative
  – How far you can push data?
  – When you should start to be suspicious?
  – How to spot problems
• Be interactive
Information in a Powder Pattern

1. Peak positions determined by size and shape of unit cell – internal structure

2. Peak Intensities determined by where atoms sit in unit cell – internal structure

3. Peak widths determined by size/strain of crystallites – microstructure.

4. Background oscillations may contain information about short range order in material

Rietveld Refinement

Observed
Calculated
Difference

Counts

2θ - degrees

Approximate Timetable

Sunday 8/4/16
08:30
09:00
11:00
Lunch – Collingwood
14:30 onwards
Registration in Collingwood College
18:30 Welcome/Intro
19:00 Pub Quiz
19:30 19.00 Symmetry tutorial
Dinner – Collingwood
20:00
21:00

Monday 9/4/16
08:45
10:00
11:45
Lunch – Collingwood
Dinner – Collingwood
"Fun" Tutorial
19.00 Bar open
19.30 Course Dinner

Tuesday 10/4/16
10:45
12:00
12:30
Lunch – Collingwood
Lunch – Collingwood
Lunch – Collingwood

Weds 11/4/16
16:00
17:30
19:00
19:30 19.00 Symmetry tutorial
Dinner – Collingwood
Dinner – Collingwood

Thursday 12/4/16
15:00
16:00
17:30
Dinner – Collingwood
Dinner – Collingwood
Dinner – Collingwood

Lecture slot
Other Practical
Registration/Free problems
Lunch – Collingwood
Lunch – Collingwood
Dinner – Collingwood

Key:
Lecture/Workshop
Other
Practical
Dinner/Open

Crystallographic Symmetry

Jeremy Karl Cockcroft
Department of Chemistry, UCL

Why bother?

• To describe crystal structures
  ➢ Simplifies the description, e.g. NaCl structure
    » Requires coordinates for just 2 atoms + space group symmetry!
• To solve crystal structures
  ➢ Relate diffraction (reciprocal-space) symmetry to crystal (real-space) symmetry
• To relate crystal structures
  ➢ Phase transitions
• To index a powder pattern
  ➢ Exploit symmetry of the unit cell

Types of Symmetry

• Rotational symmetry about a line
• Rotary-inversion symmetry about a line
• Translational symmetry
• Screw symmetry
• Glide symmetry

Rotational Symmetry

• Rotation anticlockwise 360° / n
  ➢ Symbols: 1, 2, 3, 4, 6
Symmetry Operators

- Need to distinguish between symmetry elements, symmetry operators, & coordinates

Symmetry Operators

- Advantage of non-orthogonal axes

Symmetry Operators

- Off-centre (non-origin) axes

Rotary-inversion Symmetry

- Rotation anticlockwise 360° / n + Inversion
  - Symbols: -1, -2, -3, -4, -6
    - written with bar  ¯ above digit
    - n = 1
    - enantiomorphs
Mirror Symmetry

• Rotary-inversion axis with $n = 2$

Higher-order Rotary-inversion

• Staggered v. eclipsed $C_2H_6$ -3 and -6

Translation Symmetry
Unit Cell & Lattices

- Define unit cell (6 parameters)

- Lattice obtained by adding unit translations in $x$, $y$, and $z$

Coordinate Systems

- Cartesian: $X$, $Y$, $Z$
  
  $\mathbf{r} = X\mathbf{i} + Y\mathbf{j} + Z\mathbf{k}$

- Fractional real space: $x$, $y$, $z$
  
  $\mathbf{r} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c}$

- Integer reciprocal space: $h$, $k$, $l$
  
  $\mathbf{r}^\ast = h\mathbf{a}^\ast + k\mathbf{b}^\ast + l\mathbf{c}^\ast$

7 Crystal Systems

- Combination of rotational (or rotary-inversion) symmetry with a lattice

<table>
<thead>
<tr>
<th>Crystal System</th>
<th>Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>1× 1-fold</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>1× 2-fold</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>3× 2-fold</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>1× 4-fold</td>
</tr>
<tr>
<td>Trigonal</td>
<td>1× 3-fold</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>1× 6-fold</td>
</tr>
<tr>
<td>Cubic</td>
<td>4× 3-fold</td>
</tr>
</tbody>
</table>
14 Bravais Lattices

- Combination of 7 crystal systems with lattice centring operation
  - P, A, B, C, I, F, R

Screw Symmetry

- Combination of rotational symmetry with translational: $n_m \left( 360^\circ/n \cdot R + m/n \cdot T \right)$
  - Enables efficient packing of atoms/molecules

Helical Symmetry e.g. 3₁ v. 3₂

- Others 4₁ and 4₃, 6₁ and 6₅, 6₂ and 6₄
  - Note 2₁, 4₂, 6₃ are not helical

Glide Symmetry

- Combination of 2-fold rotary-inversion ($m$) with translation: $a, b, c, n, d$
  - Also enables efficient packing of atoms/molecules
Symmetry Symbols

• Planes parallel to the screen plane

\[ \begin{align*}
  m & \quad a & \quad b & \quad n & \quad d & \quad a+b \\
  & \quad \uparrow & \quad \uparrow & \quad \uparrow & \quad \uparrow & \quad \uparrow \\
\end{align*} \]

• Planes perpendicular to the screen plane

\[ \begin{align*}
  m & \quad a & \quad c \\
  n & \quad d & \quad a+c \\
\end{align*} \]

Symmetry Symbols

• Axes perpendicular to the plane

\[ \begin{align*}
  2 & \quad 2_1 & \quad 2/m & \quad 2_{1/m} & \quad \overline{1} \\
  3 & \quad 3_1 & \quad 3_2 & \quad \overline{3} \\
  4 & \quad 4_1 & \quad 4_2 & \quad 4_3 & \quad \overline{4} & \quad 4/m & \quad 4_{2/m} \\
  6 & \quad 6_1 & \quad 6_2 & \quad 6_3 & \quad 6_4 & \quad 6_5 & \quad 6/m & \quad 6_{3/m} \\
\end{align*} \]

Symmetry Symbols

• Axes parallel or inclined to the plane of the screen

\[ \begin{align*}
  2 & \quad 2_1 & \quad 2 & \quad 2_1 \\
  3 & \quad 3_1 & \quad 3_2 \\
  4 & \quad 4_1 & \quad 4_2 & \quad 4_3 & \quad \overline{4} & \quad 4 \\
\end{align*} \]

Point Groups

• Local symmetry at a point in space
• Combination of rotation and rotary-inversion axes to form a mathematical group

➢ Only use 1, 2, 3, 4, 6 and -1, -2, -3, -4, -6
➢ 32 crystallographic point groups
   ➢ 11 centrosymmetric
       ▶ Diffraction symmetry
       ▶ Laue classes
Point Groups

- 11 centrosymmetric point groups
  - $1 \ 2/m \ 4/m \ 4/mmm$
  - $3 \ -3m \ 6/m \ 6/mmm \ m-3 \ m-3m$

- 11 enantiomorphic point groups
  - Rotation axes only
    - $1 \ 2 \ 222 \ 4 \ 422 \ 3 \ 32 \ 6 \ 622 \ 23 \ 432$

- 10 polar point groups
  - Leave more than one common point unchanged
    - $1 \ 2 \ m \ mm2 \ 4 \ 4mm \ 3 \ 3m \ 6 \ 6mm$

Example

- Combination of $m_x$, $m_y$, and $z$ gives $mm2$

Molecular Symmetry

- May be higher than crystallographic point group symmetry e.g. $C_{60}$
  - Point group $5 \ -3 \ 2/m$

Diffraction Symmetry

- e.g. $2/m$
Optical Demonstration

• Not practical to show in 3D, but easy to show in 2D using diffraction from simple “wall paper patterns” (17 possibilities)
  ➢ Objects photographically reduced to μm size on 35 mm slides
  ➢ Similar in size scale to red or green laser light
    » Expect optical diffraction to occur
      *Recall school experiment where a 1D set of parallel slits \( \rightarrow \) 1D set of spots with “orders” of diffraction

Optical Demonstration

• Note the following points:
  ➢ Inversion symmetry is added during the process of diffraction
    » Not exact as object itself has no inversion symmetry but very close to centre of symmetry
  ➢ Diffraction space unit cell vectors are in a different direction to real space ones when angle is non 90°
Optical Demonstration

• Note the following point:
  ➢ Translational symmetry along a line leads to missing intensity spots in a systematic manner along a line in a diffraction space.

Optical Demonstration

• Note the following point:
  ➢ Translational symmetry in two dimensions leads to missing intensity spots in a systematic manner in a plane in a diffraction space.
Optical Demonstration

- Note the following point:
  - 3-fold symmetry gives many problems in crystallography especially with powder diffraction as it can look like 6-fold symmetry

Diffraction Symmetry

- Crystalline objects diffract
  - Symmetry relationship between crystal (“real”) space with 3D symmetry across all space and diffraction (“reciprocal”) space with 3D symmetry at a point \((h,k,l = 0,0,0)\)
    » Not a 1:1 relationship!
- Are diffracting objects (i.e. ones that produce sharp spots) crystalline?
Space Groups

- Combination of symmetry elements to form a mathematical group
  - All must contain at least the identity (1) operation plus the unit translations:
    - \( t(1,0,0), t(0,1,0), t(0,0,1) \)
  - "Mother of All Space Groups" is \( P1 \)
- 230 combinations
  - Classified by crystal system & crystal class

Crystal Class

- Point group derived from a space group by setting all the translation components of the symmetry operators to zero
  - e.g. \( 2_1 \rightarrow 2, a \rightarrow m, ... \)
- Crystal class + Inversion symmetry
  - Diffraction symmetry

Space Group Diagrams

Special Positions

- Points in space where the symmetry is higher than 1
  - e.g. SF\(_6\)
Asymmetric Units

- Space occupied by molecule can be used!
Space Group Determination

- Geometrical implications, e.g.
  - $a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$ → triclinic
  - $a \neq b \neq c, a = \gamma = 90^\circ, \beta \neq 90^\circ$ → monoclinic
  - $a \neq b \neq c, a = \beta = \gamma = 90^\circ$ → orthorhombic
  - $a = b \neq c, a = \beta = \gamma = 90^\circ$ → tetragonal
  - $a = b = c, a = \beta = \gamma = 90^\circ$ → cubic

- Beware of experimental error
  - Symmetry may be lower than expected

Systematic Absences

- Random v. systematic zero intensity

- Beware of experimental error
  - Symmetry may be lower than expected
Systematic Absences

- Random v. systematic zero intensity

- Reflection Conditions
  \( I(h00) \neq 0 \text{ when } h = 2n \) (i.e. \( h \) even)

Centred Lattices

- Reciprocal Space v. Real Space

  - Translation in 3 dimensions gives rise to reflection condition in 3 dimensions

<table>
<thead>
<tr>
<th>P</th>
<th>none</th>
<th>none</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>( x, \frac{1}{2}+y, \frac{1}{2}+z )</td>
<td>( hkl: k + l = 2n )</td>
</tr>
<tr>
<td>B</td>
<td>( \frac{1}{2}+x, y, \frac{1}{2}+z )</td>
<td>( hkl: h + l = 2n )</td>
</tr>
<tr>
<td>C</td>
<td>( \frac{1}{2}+x, \frac{1}{2}+y, z )</td>
<td>( hkl: h + k = 2n )</td>
</tr>
<tr>
<td>I</td>
<td>( \frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}+z )</td>
<td>( hkl: h + k + l = 2n )</td>
</tr>
<tr>
<td>F</td>
<td>( A + B + C )</td>
<td>( hkl: h + k = 2n, h + l = 2n, ) &amp; ( h + k = 2n )</td>
</tr>
</tbody>
</table>
Translation Along an Axis

- No translation, e.g. 2 axis
  - No reflection condition

Translation Along an Axis

- With translation, e.g. 2₁ axis
  - Reflection condition 00l: \( l = 2n \)

Screw Axes

- Translation in 1 dimension gives rise to reflection conditions in 1 dimension:
  - 2₁ (x) \( h00: h = 2n; \) \( y0k0: k = 2n; \) \( (z) 00l: l = 2n \)
  - 3₁ or 3₂ (z) \( 00l: l = 3n \)
  - 4₁ or 4₃ (z) \( 00l: l = 4n \); 4₂ (z) \( 00l: l = 2n \)
  - 6₁ or 6₅ (z) \( 00l: l = 6n \); 6₂ or 6₄ (z) \( 00l: l = 3n \);
    - 6₃ (z) \( 00l: l = 2n \)

Glide Planes

- Translational component gives rise to reflection conditions in a diffraction plane
  - Reflection condition \( h0l: l = 2n \)
Glide Planes

• Translation in 2 dimensions gives rise to reflection conditions in 2 dimensions:

<table>
<thead>
<tr>
<th>a</th>
<th>b</th>
<th>c</th>
<th>n</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>N/A</td>
<td>0kl: k = 2n</td>
<td>0kl: l = 2n</td>
<td>0kl: k+l=2n</td>
<td>0kl: k+l=4n</td>
</tr>
<tr>
<td>h0l: h = 2n</td>
<td>h0l: l = 2n</td>
<td>h0l: h+l=2n</td>
<td>h0l: h+l=4n</td>
<td></td>
</tr>
<tr>
<td>hk0: h = 2n</td>
<td>N/A</td>
<td>hk0: k = 2n</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>etc.</td>
<td>etc.</td>
<td>etc.</td>
<td>etc.</td>
<td>etc.</td>
</tr>
</tbody>
</table>

Single-Crystal v Powder Diffraction

• Single crystal
  ➢ Lattice reflection conditions obvious
  ➢ Glide plane reflection conditions obvious
  ➢ Screw axis reflection conditions often obvious

• Powder
  ➢ Lattice reflection conditions often obvious
  ➢ Glide plane reflection conditions less obvious
  ➢ Screw axis reflection conditions very tricky

Space Groups & Standards

• 230 Space Groups for 3 Dimensions
• BUT
  ➢ Crystallographer chooses unit cell
  ➢ Crystallographer chooses an origin
    » Consequence is that many sets of symmetry operators can represent the same space group
  ✤ Number is finite (but may still be very large) if a sensible origin is chosen

Example: Space Group No.7

x, y, z & x, -y, 1/2+z
x, y, z & x, 1/2-y, 1/2+z
x, y, z & 1/2+x, -y, z
x, y, z & 1/2+x, -y, 1/2+z
x, y, z & 1/2+x, 1/2+y, -z
x, y, z & -x, 1/2+y, 1/2+z
x, y, z & -x, 1/2+y, z
x, y, z; 1/2+x, y, 1/2+z; 1/2+x, -y, z; & x, -y, 1/2+z
x, y, z; 1/2+x, y, 1/2+z; 1/2+x, -y, 1/2+z; & 1/2+x, -y, 1/2+z
• All have lattice translations plus glide plane
Need for Standards

- Comparison of crystal structures
  - Is one's structure a new structure?
  - Differences are easy to spot
    - e.g. if space group number is different then new structure is obviously different
    - Unless one had made a mistake!
  - Similarities may be much harder
Comparison Problems

Non-Standard Space Groups

• Why bother with non-standard space group settings?
  ➢ Make comparison of crystal structures in different space groups easier
  ➢ To help solve crystal structures that change as a result of a phase transition

• Are there lots of non-standard settings of space groups?
  ➢ YES

Triclinic
(For the enlarged unit cells, click here)

1. P1
2. P-1

Monoclinic
(For a fuller list with alternative unique axes, origins, or enlarged unit cells click here)

3. P1 21
4. P1 21 1
5. C1 21
6. P1 m1
7. P1 c1
8. C1 m1
9. C1 c1
10. P1 2/m1
11. P1 2/m1
12. C1 2/m1
13. P1 2/c1
14. P1 2/c1
15. C1 2/c1

Orthorhombic
(For a fuller list with alternative axes and origins click here)

16. P2 22
17. P2 22 1
18. P2 1 2 2
19. P2 1 2 2 1
20. C2 2 2
21. C2 2 2
22. P2 2 2
23. I2 2 2
24. I2 1 2 2 1
25. P m m 2
26. P m c 2 1
27. P c c 2
28. P m a 2
29. P c a 2 1
30. P n c 2

x-axial unique

3. (i) P 2 1 1 (ii) A 2 1 1
4. (i) P 2 1 1 1 (ii) A 2 1 1 1
5. (i) B 2 1 1 (ii) C 2 1 1 (iii) I 2 1 1 (iv) F 2 1 1
6. (i) P m 1 1 (ii) A m 1 1
7. (i) P b 1 1 (ii) P c 1 1 (iii) P n 1 1 (iv) A b 1 1 (v) A d 1 1
8. (i) B m 1 1 (ii) C m 1 1 (iii) I m 1 1 (iv) F m 1 1
9. (i) B b 1 1 (ii) C b 1 1 (iii) I b 1 1 (iv) F d 1 1
10. (i) P 2 / m 1 1 (ii) A 2 / m 1 1
11. (i) P 2 1 / m 1 1 (ii) A 2 1 / m 1 1
12. (i) B 2 / m 1 1 (ii) C 2 / m 1 1 (iii) I 2 / m 1 1 (iv) F 2 / m 1 1
13. (i) P 2 / b 1 1 (ii) P 2 / c 1 1 (iii) P 2 / n 1 1 (iv) A 2 / b 1 1 (v) A 2 / d 1 1
14. (i) P 2 1 / b 1 1 (ii) P 2 1 / c 1 1 (iii) P 2 1 / n 1 1 (iv) A 2 1 / b 1 1 (v) A 2 1 / d 1 1
15. (i) B 2 / b 1 1 (ii) C 2 / c 1 1 (iii) I 2 / b 1 1 (iv) F 2 / d 1 1
Non-Standard Space Groups

- Different choice of unit cell vectors
- Origin at different locations
  - See space group $I4_1/a$ on UCL web pages
    - http://pd.chem.ucl.ac.uk/sgp/large/088a.htm
- Use of enlarged unit cells
  - e.g. $F 1 2/d 1$

- Unacceptable reasons
  - Too lazy to convert to standard setting

Web Site

- 3-D Symmetry Elements
  - http://pd.chem.ucl.ac.uk/pdnn/symm1/symindex.htm
- Point Groups
  - http://pd.chem.ucl.ac.uk/pdnn/symm2/indexpnt.htm
- Space Groups
  - http://pd.chem.ucl.ac.uk/pdnn/symm3/spgindex.htm
- Space-Group Determination
  - http://pd.chem.ucl.ac.uk/pdnn/symm4/condex.htm
- Space Groups Diagrams & Tables
  - http://pd.chem.ucl.ac.uk/sgp/
Session 3: Introduction to (Powder) Diffraction
Dr Ivana Evans
Durham University

Outline
• Diffraction
• Bragg’s law and Laue equations
• Reciprocal lattice
• Ewald construction
• Atomic scattering factor
• Structure factor
• Information in a powder pattern

Historical Background
• 1895: Röntgen discovers X-rays
• 1912: von Laue discovers X-ray diffraction on crystals
• 1913: Bragg & Bragg discover structure analysis by XRD, NaCl
• 1916: Debye & Scherrer discover powder X-ray diffraction, LiF
• 1963: Zachariasen solves the structure of β-Pu from PXRD by direct methods
• 1969: Rietveld method
• 1990: direct space approaches to structure solution
• 2000: work on 100+ atom structures, proteins

Waves
➢ Basic characteristics of periodic waves
  • Amplitude, $A_0$
  • Period, $\tau$
  • Frequency, $\nu$ (angular frequency, $\omega$)
  • Wavelength, $\lambda$
  • Phase, $\phi = (kx - \omega t)$

➢ Phase relationships
  • In-phase:
  • Out-of-phase:

➢ Superposition of waves
  • Coherent waves: constant phase relationship
  • Constructive and destructive interference

Basic wave function
$$A = A_0 \cos(kx - \omega t)$$

Variation with position at one time

Variation with time at one place
Huygens Principle

- Propagation of waves:
  - Every point on a wavefront is a source of spherical wavelets
  - The developing wavefront is an envelope of these wavelets
  - The propagation direction is tangential to this envelope

Multiple Slits

- Diffraction:
  - Slit width comparable to the wavelength of the incident waves

Young’s Double Slit Experiment

- Diffraction by Crystalline Solids
  - Crystalline materials = long-range 3D periodic atomic arrays
    - Interatomic distances ~ 0.5 – 2.5 Å
  - Waves of comparable wavelengths will be diffracted
    - X-rays = EM radiation, \( \lambda \approx 0.1 \text{ – } 100 \text{ Å} \)
    - Neutrons
    - Electrons
    \[
    \lambda = \frac{h}{mv}
    \]
  - X-rays, neutrons and electrons are diffracted by crystals
  - X-ray, neutron and electron diffraction patterns contain information about 3D arrangement of atoms in crystals
1D Array of Atoms

Constructive interference:
\[(AB - CD) = a(\cos \alpha_n - \cos \alpha_o) = h\lambda\]

In vector terms: \[a \cos \alpha_n = a \cdot S, a \cos \alpha_o = a \cdot S_o,\]
Laue equation: \[a \cdot (S - S_o) = h\lambda\]
\[S_o, S = \text{incident and scattered wave vector}\]

2D Array of Atoms

Laue equations: \[a \cdot (S - S_o) = h\lambda\]
\[b \cdot (S - S_o) = k\lambda\]
simultaneous solution \(\Rightarrow\) maxima in 2 directions

3D Array of Atoms

Laue equations: \[a \cdot (S - S_o) = h\lambda\]
\[b \cdot (S - S_o) = k\lambda\]
\[c \cdot (S - S_o) = l\lambda\]
simultaneous solution \(\Rightarrow\) maxima in 1 direction

Bragg’s Law

\[2d_{hkl}\sin\theta = \lambda\]

\(2\Delta = n\lambda\)
\((n=\text{order of diffraction}^*)\)

\(*n=1, \text{because } n^{th} \text{ order diffraction from } (hkl) \text{ planes with spacing } d \text{ can be treated as }\)
\(^1\text{st} \text{ order diffraction from } (nh, nk, nl) \text{ planes with spacing } d/n\)
**Miller Indices**

- Notation used for imaginary atomic planes in crystals, \((hkl)\)
- For each set of parallel planes:
  - Take the plane closest to the one that passes through the origin
  - Write down the intercepts with the crystallographic axes (as fraction of the unit cell edges)*: \(\frac{1}{h}, \frac{1}{k}, \frac{1}{l}\)
  - Take reciprocals of these fractions to assign Miller indices, \((hkl)\)

**2D examples:**

*if a plane is parallel to a crystallographic axis, that intercept is \(\infty\)*

**d-spacings and Cell Parameters**

- d-spacings in crystals are related to the unit cell parameters \(a, b, c\)
- For orthogonal crystal systems:
  \[
  \frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}
  \]

**Applications:**

- From known unit cell parameters, we can predict diffraction patterns (peak positions)
- From experimentally observed peak positions, we can determine unit cell parameters

**Bragg’s Law: Application**

- Predicting the diffraction pattern (peak positions)
- Example: Po
  - Primitive cubic (\(Pm-3m\))
  - \(a = 3.352\ \text{Å}\)
  - \(\lambda = 1.54056\ \text{Å}\)

**Bragg’s Law: Application**

- Determining unit cell parameters (indexing the pattern)
- Example: unknown material
  - Cubic
  - 2-theta values for the first 5 observed reflections given
  - \(\lambda = 1.54056\ \text{Å}\)

*For practice: Do this by hand!*
**Reciprocal Lattice**

For a set of direct lattice vectors $a$, $b$, and $c$, reciprocal lattice vectors $a^*$, $b^*$, and $c^*$ are defined by two simultaneous conditions:

\[
\begin{align*}
    a \cdot a^* &= b \cdot b^* = c \cdot c^* = 1 \\
    a \cdot b^* &= a \cdot c^* = b \cdot a^* = b \cdot c^* = c \cdot a^* = c \cdot b^* = 0
\end{align*}
\]

It follows (in general and in orthogonal systems):

\[
\begin{align*}
    a^* &= \frac{(b \times c)}{V} \\
    b^* &= \frac{(c \times a)}{V} \\
    c^* &= \frac{(a \times b)}{V} \\
    a^* &= \frac{1}{a} \\
    b^* &= \frac{1}{b} \\
    c^* &= \frac{1}{c}
\end{align*}
\]

\[
\begin{align*}
    d_n^{\text{ReLPs}} &= \frac{1}{d_{hkl}} \\
    d_n^{\text{ReLPs}} &= \frac{h}{a^*} + k/b^* + l/c^*
\end{align*}
\]

**Ewald Construction**

\[
\begin{align*}
    d^* &= S - S_0 \quad \text{(scattering vector)} \\
    d^* &= \frac{2}{\lambda} \sin \theta \\
    \frac{1}{d} &= \frac{2}{\lambda} \sin \theta \\
    2\sin \theta &= \lambda
\end{align*}
\]

Diffraction condition is satisfied when a reciprocal lattice node intersects the Ewald sphere.

- **Ewald Sphere**
  - Shows the direction of each diffracted beam
    - Crystal in a random orientation may not give any diffraction
    - Use of polychromatic radiation
  - Shows which reflections are observable for given $\lambda$
    - Limiting sphere
    - Only ReLPs which lie within the limiting sphere will be observed
Diffraction Patterns

- Experimentally observed diffraction patterns

Single crystal diffraction  Powder diffraction

![Diffraction Patterns](image)

Scattering of X-rays by the Unit Cell

- Peak intensities, \( I_{hkl} \): \( I_{hkl} \propto |F_{hkl}|^2 \)
  - \( |F_{hkl}| \) ~ the collective scattering power of the atoms in the unit cell
  - Other factors: absorption, thermal vibrations, site occupancies, …

- Structure factor, \( F_{hkl} \)

\[
F_{hkl} = \sum_{n=1}^{N} f_n e^{2\pi i (hx_n + ky_n + lz_n)}
\]

Electronic property of the atom
Information about atom types

Structural property of the unit cell
Information about atomic positions

\(*x_n, y_n, \text{and } z_n \text{are atomic fractional coordinates: } x_n = x/a, y_n = y/b, z_n = z/c\)

Intensities – Scattering by an Atom

\[
f = \frac{\text{amplitude of the wave scattered by an atom}}{\text{amplitude of the wave scattered by one electron}}
\]

- The atomic scattering factor \( f = Z \) for any atom in the forward direction \((2\theta = 0)\)

- As \( \theta \) increases \( f \) decreases \( \rightarrow \) functional dependence of the decrease depends on the details of the distribution of electrons around an atom

- \( f \) is calculated using quantum mechanics

![Intensities – Scattering by an Atom](image)

![Pyridine-3-carboxylic acid](image)

Pyridine-3-carboxylic acid
Niacin
Nicotinic acid
Vitamin B3
Samples

(a) Single crystal

(b) Four differently oriented single crystals

(c) Polycrystalline material

(d)

2-theta

Experiment

‘…data compressed into one dimension…’

20

Powder Diffraction Can Give You

Thermal expansion

Structure determination

Kinetics studies

Particle size

Phase transitions

Particle strain

Ionic migration

In-situ chemistry

Crystallisation/amorphisation

Polymorphism
Session 6: Introduction to Least Squares

Prof John S.O. Evans
Durham University

Lecture Contents

1. Matrix revision
2. How to work out averages and standard deviations
3. How to fit a straight line to experimental data
4. How to work out standard uncertainties
5. The “correlation matrix”
6. Constraints and restraints and how they’re used
7. Thinking critically about least squares refinements
8. Non-linear least squares
9. Least squares in excel
10. Least squares in topas
11. Least squares by hand

Outline

• Least squares lies at heart of Rietveld refinement
• Some of the maths behind least squares
• Matrix language
• There will be equations!
• Watch them here…..digest at your leisure
• Several different “recipes”

• Problems in excel/topas today
• Problems on paper later/tomorrow (if you like)
• Purple/red might be minor changes on slides!

Matrix Reminders

Matrix:

\[
A = \begin{pmatrix}
  a & b \\
  c & d \\
\end{pmatrix}
\]

Inverse:

\[
A^{-1} = \frac{1}{ad - bc} \begin{pmatrix}
  d & -b \\
  -c & a \\
\end{pmatrix}
\]

\[
AA^{-1} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}
\]

Transpose:

\[
A^T = \begin{pmatrix}
  a & b & c \\
  d & e & f \\
\end{pmatrix}
\]

\[
AA^T = \text{(square)}
\]

Multiplication:

\[
B = \begin{pmatrix}
  e & f \\
  g & h \\
\end{pmatrix}
\]

\[
AB = \begin{pmatrix}
  a & b \\
  c & d \\
\end{pmatrix} \begin{pmatrix}
  e & f \\
  g & h \\
\end{pmatrix}
 = \begin{pmatrix}
  ae + bg & af + bh \\
  ce + dg & cf + dh \\
\end{pmatrix}
\]
Determining One Parameter

- Assume we've got somebody to measure male delegates' height and get the following answers:
  - 1.75, 1.79, 1.80, 1.77, 1.82, 1.60, 1.85 m
- We might decide to take an average of these measurements
- We might work out the variance (\(\sigma^2\)) and therefore the standard deviation (\(\sigma\))

\[
\sum_i w_i x_i = \bar{x} \Rightarrow \sum_i w_i = \frac{1}{\sigma^2}
\]

\[
\sigma^2 = \frac{1}{n-1} \sum_i (x_i - \bar{x})^2 = 0.0066
\]

\[
\sigma = 0.08
\]

\[
\sigma(\bar{x}) = \sigma / \sqrt{n} = 0.03 \Rightarrow \bar{x} = 1.77(3)
\]

Weighted Averages

- Male delegates' height measurements
  - 1.75, 1.79, 1.80, 1.77, 1.82, 1.60, 1.85 m
- Lets assume that the last two measurements are less reliable than the first 5 (\(\times 2\) uncertainty)
- Take a weighted average to find the "best" answer
- One way to define "best" is as the value of \(x_{av}\) which minimises the variance
- The weights to use are then inversely proportional to the variance of each individual measurement, \(\sigma_i^2\) (here \(\frac{1}{4}\))

\[
\bar{x} = \frac{\sum_i w_i x_i}{\sum_i w_i} = \frac{1}{\sum_i w_i} \sum_i w_i x_i = \frac{1}{\sigma_i^2}
\]

Least Squares

- Minimise sum of the squares of the deviations from mean
- “Least Squares”

\[
\bar{x} = \frac{\sum_i w_i x_i}{\sum_i w_i}
\]

\[
\sum_i w_i (x_i - \bar{x})^2 = \frac{\sum_i w_i}{\sigma_i^2}
\]

\[
\sum_i w_i (x_i - \bar{x})^2 = \frac{\sum_i w_i}{\sigma_i^2}
\]

- Old value (all the data) was smaller with larger variance:

\[
\bar{x} = 1.77 \quad \sigma^2 = 0.0066 \quad \sigma = 0.08
\]
Determining Two Parameters

- Assume we’ve done an experiment which yielded the following data points for \((x, y)\):
  - (1, 2), (2, 5), (3, 10), (4, 18)
- E.g. number of daffodils in flower outside
- We might plot the data to have a look at it
- We might then try and fit a straight line \(y = mx + c\) (e.g. extrapolate to day 5 or give rate of appearance as single number)
- How do we get the best fit?

Many Observations – 2 Unknowns

- We can express our measured data as a series of equations
  \(mx + c = y\)
- Problem: 4 equations, 2 unknowns
- Want: 2 equations, 2 unknowns
- Express equations in matrix format and apply a recipe

\[
\begin{pmatrix}
1 & 1 \\
2 & 1 \\
3 & 1 \\
4 & 1 \\
\end{pmatrix}
\begin{pmatrix}
m \\
c \\
\end{pmatrix}
=
\begin{pmatrix}
2 \\
5 \\
10 \\
18 \\
\end{pmatrix}
\]

Determining Two Parameters

- Two points only, line \(mx + c = y\):
  - (1, 2), (4, 18)
- Observational equations

\[
\begin{align*}
m \times 1 + c &= 2 \\
m \times 4 + c &= 18
\end{align*}
\]
- 2 equations, 2 unknowns
- Solve simultaneous equations
- \(m = 5.33, c = -3.33\)

Many Observations – 2 Unknowns

- Design Matrix
- Vector of Unknowns
- Observations

Normal equations of least squares

The Recipe:

\[
(A^tA)x = A^tb
\]
Many Observations – 2 Unknowns

\[
\begin{pmatrix}
1 & 2 & 3 & 4 \\
1 & 2 & 1 & 1 \\
3 & 1 & 1 & 1 \\
4 & 1 & 1 & 1 \\
\end{pmatrix}
\begin{pmatrix}
m \\
c \\
\end{pmatrix}
=
\begin{pmatrix}
2 \\
5 \\
10 \\
18 \\
\end{pmatrix}
\]

\[
\begin{pmatrix}
30 & 10 \\
10 & 4 \\
\end{pmatrix}
\begin{pmatrix}
m \\
c \\
\end{pmatrix}
=
\begin{pmatrix}
114 \\
35 \\
\end{pmatrix}
\]

\[
30m + 10c = 114 \\
10m + 4c = 35
\]

\[
m = 5.3 \\
c = -4.5
\]

Solving Equations - Matrices

\[
(A^T A) x = A^T b
\]

\[
x = (A^T A)^{-1} A^T b
\]

\[
\begin{pmatrix}
30 & 10 \\
10 & 4 \\
\end{pmatrix}
\begin{pmatrix}
m \\
c \\
\end{pmatrix}
=
\begin{pmatrix}
114 \\
35 \\
\end{pmatrix}
\]

\[
m = \begin{pmatrix}
0.2 \\
-0.5 \\
\end{pmatrix}, c = \begin{pmatrix}
114 \\
35 \\
\end{pmatrix}
\]

\[
m = -5.3, c = -4.5
\]

Solving Equations Graphically

\[
30m_1 + 10c_1 = 114 \\
10m_2 + 4c_2 = 35
\]

\[
m_1 = \frac{10c_1 + 114}{30} \\
m_2 = \frac{4c_2 + 35}{10}
\]

Rewrite as straight lines \( y = mx + c \)

\[
m = 5.3 \\
c = -4.5
\]

Standard Uncertainties

- We can use a simple “recipe”

\[
y = mx + c
\]

\[
\sigma_y = \sigma_m^2 x^2 + \sigma_c^2 + 2x\sigma_m\sigma_c\mu_m\mu_c
\]

\[
\sigma_m = \text{covariance} \\
\mu_m = \text{correlation coefficient}
\]

\[
\sum_{i=1}^{n} w_i (y - \text{calc}_i)^2
\]

\[
M = \left( \begin{array}{c}
\sigma_m^2 \\
\sigma_m \sigma_c \mu_m \\
\sigma_m \mu_m \\
\sigma_c^2 \\
\end{array} \right)
\]

\[
M = \frac{n}{n-p} \sum_{i=1}^{n} w_i (y - \text{obs}_i)^2 (A^T W A)^{-1}
\]

\[
\text{Number observations} \\
\text{Number parameters}
\]
**Standard Uncertainties**

\[
M = \sum w_i (y_{obs} - y_{calc})^2
\]

\[
\begin{pmatrix}
A^T W A
\end{pmatrix}^{-1} = \begin{pmatrix}
30 & 10 \\
10 & 4
\end{pmatrix}^{-1} = \begin{pmatrix}
0.2 & -0.5 \\
-0.5 & 1.5
\end{pmatrix}
\]

\[
\begin{array}{|c|c|c|c|}
\hline
x & yobs & ycalc & (yobs - ycalc)^2 \\
\hline
1.0 & 2 & 0.800 & 1.200 \\
2.0 & 5 & 6.100 & 1.210 \\
3.0 & 10 & 11.400 & 1.960 \\
4.0 & 18 & 16.700 & 1.690 \\
\hline
\end{array}
\]

\[
M = \frac{4}{2} \times \frac{6.3}{4} \times \begin{pmatrix}
0.2 & -0.5 \\
-0.5 & 1.5
\end{pmatrix} = \begin{pmatrix}
0.63 & -1.575 \\
-1.575 & 4.725
\end{pmatrix} = \begin{pmatrix}
\sigma_m^2 & \sigma_m \sigma_c \mu_{mc} \\
\sigma_m \sigma_c \mu_{mc} & \sigma_c^2
\end{pmatrix}
\]

\[
\sigma_m = 0.79 \\
\sigma_c = 2.17 \\
\mu_{mc} = -0.91
\]

\[
m = 5.3(8) \\
c = -4.5(20)
\]

**Correlations in Least Squares**

- Gradients and intercepts will show a negative correlation
- As gradient decreases intercept will increase

**Constraints and Restraints**

- Constraints are pieces of information your model must obey mathematically
- Restraints are "soft" information you’d like your model to obey

- [how to upset teachers/tutors: "I’ve refined the data….."]

**Constraint: Must Pass through Origin**

- Assume line must pass through origin

\[
m \times x + 0 = y
\]

\[
\begin{pmatrix}
1 & 2 & 3 \\
2 & 3 & 4
\end{pmatrix} \begin{pmatrix}
m \\
1 \\
2
\end{pmatrix} = \begin{pmatrix}
5 \\
10 \\
18
\end{pmatrix}
\]

\[
30m = 114 \\
m = 3.8(5)
\]

\[
y = 3.8x
\]
**Constraint: intercept = -gradient**

- Assume line intercept = -gradient

\[
mx \times m = y \\
m(x-1) = y
\]

- \[ m \times 0 = 2 \]
- \[ m \times 1 = 5 \]
- \[ m \times 2 = 10 \]
- \[ m \times 3 = 18 \]

\[
\begin{bmatrix}
0 & 1 & 2 & 3 \\
1 & 2 & 3 & 4 \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1 \\
0 & 0 & 0 & 0
\end{bmatrix}
\begin{bmatrix}
2 \\
5 \\
10 \\
18 \\
35 \\
0
\end{bmatrix}
= 
\begin{bmatrix}
0 \\
30 \\
10 \\
0
\end{bmatrix}
\]

\[
14m = 79 \\
m = 5.6(4) \\
c = -5.6(4)
\]

**Restraint – "Must" Pass through Origin**

- Treat \( x = 0, y = 0 \) as an extra observation

\[
\begin{bmatrix}
1 & 1 \\
2 & 1 \\
3 & 1 \\
4 & 1 \\
0 & 1
\end{bmatrix}
\begin{bmatrix}
m \\
c
\end{bmatrix}
= 
\begin{bmatrix}
2 \\
5 \\
10 \\
18 \\
10m + 5c = 35
\end{bmatrix}
\]

\[
30m + 10c = 114 \\
10m + 5c = 35
\]

\[
m = 4.4 \\
c = -1.8
\]

**Restraint – "Must" Pass through Origin**

- Treat \( x = 0, y = 0 \) as an extra observation, but give a high weight

\[
W_Ax = W_b
\]

\[
(A^TWA)x = (A^TW)b
\]

\[
\begin{bmatrix}
1 & 1 & 2 & 3 & 4 & 0 \\
0 & 1 & 0 & 0 & 0 & 3 \\
0 & 0 & 1 & 0 & 0 & 4 \\
0 & 0 & 0 & 1 & 0 & 3 \\
0 & 0 & 0 & 0 & 100 & 0
\end{bmatrix}
\begin{bmatrix}
1 \\
0 \\
0 \\
0 \\
0
\end{bmatrix}
= 
\begin{bmatrix}
1 \\
2 \\
0 \\
0 \\
0
\end{bmatrix}
\]

\[
\begin{bmatrix}
1 & 1 & 2 & 3 & 4 & 0 \\
0 & 1 & 0 & 0 & 0 & 3 \\
0 & 0 & 1 & 0 & 0 & 3 \\
0 & 1 & 0 & 0 & 0 & 4 \\
0 & 0 & 0 & 1 & 0 & 3 \\
0 & 0 & 0 & 0 & 100 & 0
\end{bmatrix}
\begin{bmatrix}
m \\
c
\end{bmatrix}
= 
\begin{bmatrix}
2 \\
5 \\
10 \\
18 \\
0
\end{bmatrix}
\]

\[
30m + 10c = 114 \\
10m + 104c = 35
\]

\[
m = 3.81 \\
c = -0.03
\]

**Standard Uncertainty = ????**
Appropriate Model/Data Quality

- Need good quality data but also data that defines the problem you’re trying to answer
- Feynman’s rule

\[ y_{\text{obs}} = Y_C - y_{\text{calc}} \]

Non Linear Least Squares

- We have a recipe for linear least squares for simple expressions like \( y = mx + c \)
- In crystallography equations will be more complex, e.g.
  \[ Y_C = \sum_{j=1}^{N} f_j \exp\left[2\pi i (hx_j + ky_j + lz_j)\right]^2 \]
- Let’s assume that calculated intensity, \( Y_C \), is a function of several variables \( x_i \)
  \[ Y_C = f(x_1, x_2, x_3, \ldots, x_{\text{gp}}) \]
- If we guess values for \( x_i \) and calculate the intensity the chances are it won’t match observed intensity, \( Y_O \):
  \[ Y_O - Y_C \neq 0 \]

Non Linear Least Squares

\[ Y_O - Y_C \neq 0 \]

- We’d like to know how much to change each \( x_i \) variable by in order to make \( Y_O - Y_C \) zero
- If we knew these \( \delta x_i \) values we could then just change our guesses and the calculated intensity would be correct
- We can write a Taylor series for this:
  \[ \frac{\partial Y}{\partial x_1} \delta x_1 + \frac{\partial Y}{\partial x_2} \delta x_2 + \ldots + \frac{\partial Y}{\partial x_{\text{gp}}} \delta x_{\text{gp}} = Y_O - Y_C \]
- Equation is just like \( mx + c = y \) and is linear in the shifts \( \delta x_i \)
- One equation like this for each observed intensity \( Y_O \)
- We can write the equation in matrix format
  \[ A \cdot \delta x = y \]

Non Linear Least Squares

- In full this expression looks complicated:

\[ A \cdot \delta x = y \]

\[ (A^T A) \delta x = A^T \cdot y \]

- We can solve it in exactly the same way

\[ \delta x = (A^T A)^{-1} A^T \cdot y \]

- We now know the shifts to apply to each parameter \( x_i \) in order to change \( Y_C \) to be the same as \( Y_O \)

\[ x_{\text{new}} = x_{\text{old}} + \delta x \]
Non Linear Least Squares - Summary

- If we have an initial set of guesses for parameters we can determine how much to change them by to make $Y_C$ and $Y_O$ the same
- Recipe only works for infinitesimally small shifts
- We may have to repeat the process several times
- We need good starting values
- This is structure refinement
- The maths is tedious and slow – use a computer

ill Conditioned Least Squares

- Consider the following equations which are just like the equations we came across earlier for fitting a straight line through data
- $m = 5.3$, $c = -4.5$ are exact solutions to the equations
- $m = 5.3$
  $c = -4.5$

Imagine we repeat the measurement and find that 114.0 in our equations changes to 114.1

- A very small change
- Solve the equations again $m = 20.5$, $c = -50$
- Oh dear!

Solving equations graphically

2 equations
2 unknowns

Rewrite as straight lines $y = mx + c$

ill Conditioned Least Squares

- $m_1 = \frac{10c_1 + 114}{30}$
- $m_2 = \frac{4c_2 + 35}{10}$
- $m = 5.3$
- $c = -4.5$
ill Conditioned Least Squares

\[
M = \begin{pmatrix}
\sigma_m^2 & \mu_{mc} \\
\mu_{mc} & \sigma_c^2
\end{pmatrix}
\]

\[
M = n \sum_i^n w_i (obs - calc)^2 (A^TWA)^{-1}
\]

\[
(A^TWA)^{-1} = \begin{pmatrix}
30.0 & 10.00 \\
10.00 & 3.34
\end{pmatrix}^{-1} = \frac{1}{100.2} \begin{pmatrix}
3.34 & -10 \\
-10 & 30
\end{pmatrix} = \begin{pmatrix}
16.7 & -50 \\
-50 & 150
\end{pmatrix}
\]

\[
\begin{pmatrix}
a & b \\
c & d
\end{pmatrix}^{-1} = \frac{1}{ad-bc} \begin{pmatrix}
d & -b \\
-c & a
\end{pmatrix}
\]

- Determinant is 0.2 – small vs contents of normal matrix
- Large errors
- Either an infinite number of solutions or no solution
- Determinant = 0 means a singular matrix

Rietveld Refinement - Definition

- Powder Pattern as 2\(\theta\)obs, \(y_{obs}\), \(\sigma(y_{obs})\)
- Cell parameters to predict positions
- Structural model \(x, y, z, uiso/adps\)
- Model to fit observed peak shapes
- Functions to describe instrument
- Functions to correct systematic effects (LP, Absorption)
- Calculate pattern \(y_{calc}\) at each \(y_{obs}\), compare fit, refine all aspects of model
- Weight using \(1/\sigma^2\)

Weighting in Rietveld refinement

- Old data formats were 2\(\theta\), Intensity
- Assume Poisson statistics \(\sigma(I) = I^{0.5}\) and weight accordingly
- For many PSD/neutron/tof/other measurements this will not hold
- Always use 2\(\theta\), Intensity, \(\sigma(I)\) format
- .xye file or equivalent gsas/fullprof
- Never e.g. convert from gsas to xy format in fullprof in a way that loses errors
- Particularly for time of flight data
- If you manipulate a file (e.g. variable to fixed slit correction) always correct errors accordingly

Agreement Indicators

- Visual inspection

\[
R_{wp} = \left( \sum_i^n w_i [y_i(\text{obs}) - y_i(\text{calc})]^2 \right)^{1/2} \]

\[
R_{exp} = \left( \sum_i^n w_i y_i^2 \right)^{1/2}
\]

\[
\chi^2 = \left( \frac{R_{wp}}{R_{exp}} \right)^2
\]

- (background biased)
- (model biased)
Least Squares in Excel

- Demonstration
- Fit our function using “chart/add trendline”
- Fit using solver
- Change to a quadratic function

Least Squares in Topas

- e.g. fit data.xy using a simple linear equation
- Calculate esd’s and correlation
- Identical to values calculated by hand
- Much easier!!

Topas/jEdit Interface

Topas Graphics

Grid
Run
Zoom
Plot
Fixing Parameters – Using !

\[
\begin{align*}
\text{prm m} & \quad 1.65 \\
\text{prm !c} & \quad 0.50 \\
\text{fit_obj} & = m \times X + c;
\end{align*}
\]

- Gradient defined as parameter \( m \) (refining)
- Intercept defined as parameter \( c \) (not refining)

Initial Software Setup

- First time you log in you’ll need to select “Rietveld Setup” in the start menu.
- Wait a few minutes for software to be copied
- Use desktop icons created (e.g. jedit_net)
- Tutorials all at: http://community.dur.ac.uk/john.evans/topas_workshop/pcg_workshop_menu.htm
- Only launch topas once from jEdit (or we’ll run out of licences)
- Use directory school_work – don’t save files in Topas directory
- [fullprof not installed by default – see later tutorials]

Problem Session

- Problems (excel)
  - Fit a linear function as in lecture
  - Fit a Gaussian peak shape
  - Perform a Pawley refinement in excel
  - Perform a full Rietveld refinement in excel
  - Refine unit cells from the morning’s tutorials

- Problems (topas)
  - Perform the same fits as in excel to compare results
  - Do it mechanically today – explanations tomorrow!
Peak Intensities in Powder Diffraction

Jeremy Karl Cockcroft
Department of Chemistry, UCL

Peak Intensities

• For an ideal powder sample:

\[ I(hkl) = c L(2\theta) P(2\theta) A(2\theta) j_{hkl} |F(hkl)|^2 \]
Polarisation

Absorption

- Reflection
- Transmission

X-Ray Mass Absorption (Cu)

X-Ray Transmittance

Transmittance through 0.2 mm assuming 50% powder packing

Cu(λ) Mo(λ)
Neutron Absorption X-Section

Structure Factors

\[ I(hkl) = k |F(hkl)|^2 \]
\[ F(hkl) = \sum s_n o_n \exp(2\pi i (hx + ky + lz)) \exp(-W_n) \]

- Vector quantity (magnitude \( F \) & phase \( \varphi \))
  - atomic scattering length \( s_n \)
  - atomic occupation \( o_n \)
  - wave interference term: \( \exp(2\pi i (hx + ky + lz)) \)
  - Debye-Waller factor \( W_n \)
- Summation over all atoms in unit cell

Structure Factors

\[ F(hkl) = \sum s_n o_n \exp(2\pi i (hx + ky + lz)) \exp(-W_n) \]

- Real Space (Crystal) ↔ Reciprocal Space (Diffraction)
- Atoms \( \otimes \) Scattering Factor \( \times \)
- Lattice \( \otimes \) Interference Term \( \times \)
- Atomic Displacements \( \otimes \) Debye-Waller Factors

- Fourier transform of \( F \) is simply the electron density (for X-ray \( F \) values)

Atomic Scattering Length \( s_n \)

- X-rays:
  - Scattering factor \( f \)
- \( s_n = \) Scattering length divided by \( r_e \)
- where \( r_e \) classical electron radius = 2.818 fm

- Neutrons:
  - Scattering length \( b \)
Scattering Length Comparison

<table>
<thead>
<tr>
<th>Element</th>
<th>H</th>
<th>D</th>
<th>U</th>
<th>Fe</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray ( f(0^\circ) (Z) )</td>
<td>1</td>
<td>1</td>
<td>92</td>
<td>26</td>
<td>27</td>
</tr>
<tr>
<td>Neutron ( b (\text{fm}) )</td>
<td>-3.74</td>
<td>6.67</td>
<td>8.42</td>
<td>9.45</td>
<td>2.78</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Ba</th>
<th>O</th>
<th>V</th>
<th>Ti</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray ( f(0^\circ) (Z) )</td>
<td>56</td>
<td>8</td>
<td>23</td>
<td>22</td>
<td>40</td>
</tr>
<tr>
<td>Neutron ( b (\text{fm}) )</td>
<td>5.28</td>
<td>5.81</td>
<td>-0.38</td>
<td>-3.44</td>
<td>5.28</td>
</tr>
</tbody>
</table>

Absolute comparison: \( f(2\theta = 0^\circ) \times r_e \)

where \( r_e = 2.818 \text{ fm} \)

Scattering as a Function of \( 2\theta \)

- X-ray interacts with electron cloud
  - Atoms are similar in size to wavelength
  - Fourier transform of the electron cloud corresponds to the X-ray form factor
    - e.g. F.T. Gaussian (broad) → Gaussian (narrow)
    - Usually tabulated as a sum of 4 Gaussians + \( c \)
Scattering as a Function of $2\theta$

- Neutron interacts with nucleus
  - Nucleus is very small (point scatterer) compared to $\lambda$
  - Fourier transform of a delta function is a horizontal line
    → No form factor for neutrons
  - Exception: interaction with unpaired electron(s)
  - Form factor for magnetic cations (e.g. Fe$^{3+}$, Ni$^{2+}$, Ho$^{3+}$) in magnetic crystallography
    - Differences in shape between TM and Ln/An elements due to differences in $d$ and $f$ orbitals

Anomalous Scattering

$$f = f_0 (2\theta) + \Delta f' + i \Delta f''$$

- Due to absorption (near edge leads to fluorescence background)

Site Occupation $o_n$

- Structure: list of atoms in asymmetric unit
- Summation performed by all applying symmetry operators to all $hkl$
  - Mathematically equivalent to applying them to all atoms
    - $o_n$ compensates for atoms on special positions since calculation assumes general position $x, y, z$
    - $o_n$ takes into account atomic disorder
**Interference Term** $e^{2\pi i (hx + ky + lz)}$

- Vector dot product between real- and reciprocal-space vectors:
  - $(ha^* + kb^* + lc^*) \cdot (xa + yb + zc)$
- Effected by translational symmetry
  - Leads to reflection conditions & systematic absences
- Not a smooth function of $2\theta$
  - Reflections with similar $d$ spacings may have large or small interference terms

**Structure Factor for NaCl**

Na$^+$ at $0,0,0; \frac{1}{2},\frac{1}{2},0; \frac{1}{2},0,\frac{1}{2}; 0,\frac{1}{2},\frac{1}{2}$
Cl$^-$ at $\frac{1}{2},\frac{1}{2},\frac{1}{2}; \frac{1}{2},0,0; 0,\frac{1}{2},0; 0,0,\frac{1}{2}$

$f_{Na}\{\cos 2\pi(h0+k0+l0) + \cos 2\pi(h\frac{1}{2}+k\frac{1}{2}+l0) + \cos 2\pi(h\frac{1}{2}+k0+l\frac{1}{2}) + \cos 2\pi(h0+k\frac{1}{2}+l\frac{1}{2})\} + f_{Cl}\{\cos 2\pi(h\frac{1}{2}+k\frac{1}{2}+l\frac{1}{2}) + \cos 2\pi(h\frac{1}{2}+k0+l0) + \cos 2\pi(h0+k\frac{1}{2}+l0) + \cos 2\pi(h0+k0+l\frac{1}{2})\}$

Note: $i \sin 2\pi(hx+ky+lz) = i \sin(n\pi) = 0$

**Interference Term** $e^{2\pi i (hx + ky + lz)}$

- May be written as a sum of cosine and sine terms:
  - $\exp(2\pi i (hx + ky + lz)) = \cos 2\pi(hx + ky + lz) + i \sin 2\pi(hx + ky + lz)$
- If atom on $x,y,z$ and on $-x,-y,-z$, then the cosine terms double and sine terms vanish
  - Use of centrosymmetric origin
    - Reduces calculation time by 50%
      - Very important when done by hand!!!!

**Structure Factor (cont)**
Debye-Waller Factors

- Atomic displacement parameters (ADPs)
- "Temperature factors"

Functions

- Isotropic (spheroid)
  \[
  \exp(-B_n \sin^2 \theta / \lambda^2) = \exp(-B_n / 4d^2) = \exp(-2\pi^2 U_n / d^2)
  \]
  - \(U_n\) is mean-square atomic displacement
  - \(B_n\) often liked since values are around 1
  - but now rarely used for SXD

- Anisotropic (ellipsoid)
  \[
  \exp(-\{\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{23}kl + 2\beta_{13}hl + 2\beta_{12}hk\})
  \]
  - Tensor quantity with 6 parameters
  - \(\beta\) used for speed of calculation but doesn’t easily relate to atomic displacements
  - contain terms relating to cell parameters
  - Use of \(b_{11}\) and \(u_{11}\) etc. (similar to \(B\) and \(U\))
    - \(b_{11} = 8\pi^2 u_{11}\)
    - independent of lattice parameters

Symmetry Constraints

- Only affected by point-group symmetry elements
  - \(u_{13} = u_{23} = 0\)
  - should always be applied by software!
Rietveld Refinement

- Objective is to refine a model structure against a measured powder diffraction pattern.
- Peak intensities provide the information about the crystal structure.
  - Peak positions provide unit cell information.
  - Peak widths and shape provide information on instrument and crystallinity of sample.

Agreement Tests

- Need to monitor progress of fit.
- Need to compare different model fits.
- Need to measure data quality.
- Solution:
  - Visualisation (XY plot)
  - Numeric quantity (popular for working blind!)
  - Monitor chemical parameters (bond lengths, angles, etc.).

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

One formula, but many interpretations.

\[ R_{\text{exp}} = \left[ \frac{(N - P + C)}{\sum w_i y_i^{\text{obs}}^2} \right]^{1/2} \]

- Other \( R \)-factors similar to \( R_{wp} \) in format:
  - \( I(hkl) \) [or even \( I(hkl)^2 \)]
  - \( |F(hkl)|^2 \)
  - \( |F(hkl)| \) etc.
  - All use derived “observed” values.

\( R_{wp} = 8.1\% \) or \( 2.5\% \) or \( 1.8\% \)!
Simple Example

- PbSO₄ at RT (powder neutron diffraction)
  - Simple structure & a model example
- Structure:
  - Space group $Pbnm$
  - $a = 7.0$ Å, $b = 8.5$ Å, $c = 5.4$ Å
  - 4 Pb (0.15,0.20,¼); 4 S (0.20,0.50,¾);
  - 4 O(1) (0.10,0.60, ¾); 4 O(2) (0.00,0.30,¾);
  - 4 O(3) (0.30,0.40,0.98)
  - $\lambda = 1.909$ Å, $U = 0.2^\circ$, $V = -0.5^\circ$, $W = 0.5^\circ$

$R_{wp} = 100\%$

- Refined scale factor $c$
  - $R_{wp} = 81\%$

- Refined unit cell parameters & $2\theta$ zero error
  - $R_{wp} = 61\%$
Refined $x,y,z$ for $O(3)$

$R_{wp} = 42.4\%$

Refined $x,y$ for Pb $O(1)\ O(2)$

$R_{wp} = 29.4\%$

Refined $x,y$ for $S$

$R_{wp} = 12.2\%$

Refined $UVW$ & $B$ (overall)

$R_{wp} = 6\%$
Final Message

• Be very self critical about the quality of your powder diffraction data fits
  - Are you getting the most out of your data?
  - Is your model correct?
• Peak positions
  - Cell size
• Peak intensities
  - Cell contents
Session 10: Basics of PXRD Data Collection
Dr Ivana Evans
Durham University

Outline

• Common laboratory configurations
• How to collect (laboratory) data
• Common sample preparation “crimes”
• Factors that affect peak positions
• Factors that affect peak intensities

Laboratory XRD Configurations

Reflection geometry

Transmission geometry

Optics:
DS: divergence slits
SS: Soller slits
AS: anti-scatter slits
RS: receiving slits

DS, AS: limit the in-plane (equatorial) divergence
SS: limit the out-of-plane (axial) divergence
Typical Optics

Laboratory Bragg Brentano

Reflection Geometry: Why Does It Work?

Parafocusing Geometry

The Law of Reflection

Euclid

Book 3,

Proposition 21

The Law of Reflection

Focusing circle

Goniometer circle

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Capillary Transmission Mode

- Important to consider capillary size — absorption and (sometimes) resolution
- Want $\mu r < 1.5$, $r =$ capillary radius
- Mass attenuation coefficients quoted as $\mu/\rho$ in cm$^2$/g

$$\mu_{\text{cpd in capillary}} = \mu_{\text{cpd}} \sum_{\text{elements}} \text{wtfrac}_{\text{element}} \times (\mu/\rho)_{\text{element}} \times \text{packing fraction}$$

Experimental Set-up

- Experiment aims should inform sample preparation, instrument configuration and data collection protocol
  - Phase identification: rapid data collection in a limited d-spacing range
  - Indexing: internal standard
  - Structure solution: broad d-spacing range; high resolution; high intensity
  - Rietveld refinement: highest quality in time available
- PXRD sample must be:
  - An ensemble of an “infinite” number of randomly oriented crystallites
  - Representative of the bulk

Data Collection

- Instrument dependent
- Consider optical set-up and whether it’s suited for your experiment. Ensure statistics are good enough for information you need
- Consider spending longer counting at higher $2\theta$ to compensate for intensity fall-off in diffraction
- Make sure you have sufficient points to define a peak (e.g. 10 across fwhm) – can rebin later but can’t create extra points
- First guess on a “normal” lab instrument
  - $5-90^\circ$ 0.02$^\circ$ step, 1 second per step ~ 1 hr

Sample Preparation

- Grinding:
  - Ensures sample homogeneity
  - Decreases crystallite size
- Possible options:
  - Mortar and pestle
  - Planetary mill
  - McCrone micronising mill
- Possible problems:
  - Structural phase transitions (small organics)
  - (Partial) amorphisation
  - Strain-induced peak broadening

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  - Strain-induced peak broadening
Sample Preparation

- Flat plate sample holders:
  - Bulk
  - Sprinkled
- Single crystal Si wafers for low background

Common Crimes – Sample Prep

- Sample height: sample displaced off the goniometer axis
  \[ \theta_{\text{offset}} = \text{zero} - 2*\Delta\text{height} \times \cos(\theta)/\text{radius}; \]

Common Crimes – Sample Prep

- Surface roughness
- Intensities affected as \( f(2\theta) \): low angle intensities reduced
- Negative temperature factors

Common Crimes – Sample Prep

- Need an “infinitely” thick sample; otherwise, intensities affected as \( f(2\theta) \)
- Thick sample: constant volume probed as \( f(2\theta) \)
- Thin sample: diffraction volume varies with \( f(2\theta) \)
Infinite Sample Thickness

- Intensity diffracted from depth $x$ in the sample:

$$ I_x \propto \frac{I_0}{\sin \theta} \exp\left(-2\mu x / \sin \theta\right) $$

- What is negligible diffracted intensity?

$$ \frac{I_{(x=0)}}{I_{(x=t)}} = 1000 $$

Common Problems – Sample Prep

- Preferred orientation: e.g. platelets with c-axis perpendicular to sheets will give strong 00l reflections

- Avoiding preferred orientation
  - Capillary measurements
  - Flat plate reflection & transmission
  - Side/back mounting
  - Spray drying
  - Sieving
  - Neutron diffraction

- Texture
  - Much harder to correct
  - Certain unrelated hkl reflections wrong intensity
Common Crimes – Data Collection

- The area the beam is incident upon must fall within the sample for all \( f(2\theta) \), otherwise beam overspill.

- Intensities affected as \( f(2\theta) \): at low \( 2\theta \) smaller volume probe, hence reduced intensities.
- High background at low \( 2\theta \) due to sample holder.

Variable Slits

- Modern diffractometers often have variable slits to compensate for this effect. Slits get larger with \( 2\theta \).

- \( \sin(\theta) \) correction.
- Don’t assume Poisson statistics as intensities manipulated.

Common Lab Problems

- Poorly aligned incident beam monochromator could give K\( \alpha_1 \) and small amount of K\( \alpha_2 \).
- Modern linear position sensitive detectors often pick up small amounts of Cu K\( \beta \) (1.392 Å) radiation if Ni foil too thin.
- Old X-ray tubes often give small amounts of W L\( \alpha \) (1.476 Å) radiation.

Factors That Affect Peak Positions

\[
2\theta_{\text{obs}} = 2\theta_{\text{calc}} + \Delta 2\theta
\]

\[\Delta 2\theta = \frac{p_1}{\tan 2\theta} + \frac{p_2}{\sin 2\theta} + \frac{p_3}{\tan \theta} + p_4 \sin \theta + p_5 \cos \theta + p_6\]

- \( p_1/p_2 \): incident beam axial divergence; peak asymmetry (\( p_1 \))
  - axial divergence corrected by using Soller slits
  - peak asymmetry due to the finite detector receiving slit length
- \( p_3 \): incident beam in-plane divergence
  - due to sample zero-curvature; small (negligible) effect
- \( p_4 \): absorption (transparency shift error)
  - due to penetration of X-rays into sample; \( p_4 = (2\mu_{\text{eff}}R)^{-1} \)
  - important for thick (>50-100\( \mu \)) samples with low absorption coefficients
- \( p_5 \): sample displacement
  - due to specimen displacement off the goniometer axis
- \( p_6 \): zero error
  - due to instrument misalignment (improper settings of source/detector zero angles)
Factors That Affect Peak Intensities

\[ I_{hkl} = K \times |F_{hkl}|^2 \times P_{hkl} \times E_{hkl} \times T_{hkl} \times (LP)_{hkl} \times A_{hkl} \times DW_{hkl} \]

- K: scale factor
- \( F_{hkl} \): structure factor
- \( P_{hkl} \): multiplicity
- \( E_{hkl} \): extinction
- \( T_{hkl} \): preferred orientation
- \( (LP)_{hkl} \): Lorentz-polarisation factor
- \( A_{hkl} \): absorption
- \( DW_{hkl} \): Debye-Waller factor

Conclusion

- Experimental set-up depends on:
  - the aims of the experiment
  - sample
  - instrument available

- Don't waste time analysing poor, inadequate or unsuitable data
Laboratory X-ray source


Bremsstrahlung (background) + electronic transitions

Cu Kα emission spectrum

Advantages of a laboratory instrument

- It's yours. It's available. No long wait to use it.
- Modern instruments are adaptable and have good precision and resolution.
- Manufactured to defined specifications.
- Sample environments and ancillary equipment are commercially available.
- Delivered with useful software, e.g. search and match / phase analysis, Rietveld refinement, etc.
Limitations of a laboratory instrument

- Limited $2\theta$ resolution, (divergent beams, low X-ray spectral purity).
- Maybe suffer from $\alpha_1\alpha_2$ doublets (unless you have a pre-sample monochromator).
- Limited to fixed wavelengths, CuK$\alpha$, MoK$\alpha$.
- Modest flux.
- Aberrations due to specimen transparency, surface effects, sample misalignment, etc.
- Limited adaptability.

Transparency aberration

- Penetrating beam spatially shifted with respect to the ideal beam path ⇒ aberration in $2\theta$ (and peak shape)

Debye–Scherrer geometry susceptible to aberrations

- Beam spatially shifted with respect to the ideal beam path ⇒ aberration in $2\theta$

Synchrotrons
- APS, Argonne, 7 GeV
- Shanghai, 3 GeV
- Petra, 6 GeV
- Australia, 3 GeV
- SINQ+SLS, 2.4 GeV ring
- ISIS+Diamond, 3 GeV ring
**Synchrotron radiation and powder diffraction**

High intensity, collimation and λ tunability

- High angular resolution, i.e. narrow peak widths;
- Rapid data collection / good statistics;
- Highly monochromatic X-rays (no α1,α2 doublets);
- Narrow well defined instrumental peak shape;
- Tunable: measure at absorption edges, or well away; optimise for the experiment;
- Hard energies for increased Q range or penetrate through absorbing samples or sample environments

**Storage ring energy = an orbiting electron’s total energy**

Electron at rest: \[ E_e = m_e c^2 \]
\[ = 8.18710564965 \times 10^{-14} \text{ J} \]
\[ = 5.109989463 \times 10^5 \text{ eV} \]
\[ = 5.109989463 \times 10^{-4} \text{ GeV} \]

\( m_e = \) electron rest mass = 9.10938356(11)×10^{-31} kg
\( c = \) speed of light = 299792458 m s^{-1}

Electron at speed \( v \): \[ E_e = \gamma m_e c^2 \]

where \[ \gamma = \frac{1}{\sqrt{1-(v^2/c^2)}} \]
Storage ring energy = an electron’s total energy

\[ E_e = 1 \text{ GeV} = \gamma \times 5.109989463 \times 10^{-4} \text{ GeV} \]
\[ \Rightarrow \gamma \approx 1957 \times E_e \text{ [GeV]} \]

- 6 GeV \[ \Rightarrow \gamma = 11742 \Rightarrow v = 0.999999964 \times c \]
- ESRF circumference = 844 m
- Electron lap time = 2.82 \( \mu \)s, so 355036 laps s\(^{-1} \)
- Current per electron = 355036 e s\(^{-1} \) \approx 56.9 \times 10^{-15} \text{ A} 
- Ring current of 200 mA \equiv 3.5 \times 10^{12} \text{ electrons.}

Synchrotron radiation

Emitted tangentially when charged particles follow a curved path at relativistic speeds

Bending magnet

ESRF bending magnet spectrum

\[ \lambda \text{[Å]} \approx \frac{12.4}{\varepsilon \text{[keV]}} \iff \varepsilon \approx \frac{12.4}{\lambda \text{[Å]}} \times 10^7 \text{ eV} \]

\[ \text{Flux / } \Delta \varepsilon = \text{[photons/(mm x mrad x 0.1% bw)]} \]

\[
\begin{align*}
\text{Photon Energy / keV} & \quad 0 & \quad 20 & \quad 40 & \quad 60 & \quad 80 & \quad 100 \\
\text{Flux / } \Delta \varepsilon & \quad 0 & \quad 1.0 & \quad 2.0 & \quad 3.0 & & \\
\end{align*}
\]
Insertion devices

Wigglers and undulators are arrays of magnets that cause the electron path to oscillate and emit radiation.

Ex-vacuum and in-vacuum undulators

$G =$ variable gap between poles to tune magnetic field

ESRF (6 Gev) u35 undulator, $G = 11$ mm gap

undulators have high vertical and horizontal collimation

Photon Energy / keV

0 20 40 60 80 100

0 2 4 6 8 10

0.2 Å
**Double-crystal monochromator**

Crystal 2 is aligned with crystal 1 to transmit $\lambda$ by diffraction.

Highly collimated, monochromatic

Crystal 1 (e.g. Si) selects $\lambda$ by diffraction, i.e.

$$\lambda = 2d_{hkl}\sin\theta_m$$

e.g. 111 planes

**ESRF ID22 Powder Diffractometer**

**Capillary sample spinner**

**Nine channel multianalyser stage**

9 detectors

9 Si 111 analyser crystals

Sample

Thanks to J.-L. Hodeau, M. Anne, P. Bordet, A. Prat, CNRS Institut Néel, Grenoble
High resolution + minimises aberrations

Analyser crystal

Defines a true $2\theta$ angle rather than inferring $2\theta$ from the position of a slit or pixel of a PSD.

- Narrow peaks (sample-limited) with accurate positions
- Peak positions insensitive to misalignment, transparency, specimen size/shape/surface effects, etc.
- Widths independent of any $\theta/2\theta$ parafocusing condition
- Supresses fluorescence, Compton, parasitic scatter.
- But relatively SLOW as it needs to be scanned and transmits photons only within the narrow "Darwin width" of the analyser crystal – (hence 9 in parallel)

High intrinsic angular resolution

Beamline I11 at Diamond, 45 analyser crystals

Si 111 peak

$\lambda \approx 0.4$ Å (31 keV)

(ESRF)
Accurate data

- Peak positions ⇒ indexing, strain, etc.
- Spinning capillaries ⇒ more-accurate intensities (less preferred orientation).
- Can choose $\lambda$ and capillary size so $\mu r < 1.5$
- Usually choose $\lambda < 1 \text{ Å}$
- At ESRF we routinely work with $\lambda \approx 0.3 - 0.4 \text{ Å}$.

Capillary: scattered intensity vs $\mu r$

Transmission decreases with absorption, $e^{-2\mu r}$

Sample volume increases with $\pi r^2$

$\mu$ = linear absorption coefficient
$r$ = capillary radius

Lysozyme
Robotic sample changer

See our YouTube video

Up to 75 samples, in 5 banks of 15

Capillaries can be prepared in advance by 15, on a lightweight plastic support.

Powder Diffraction = Sample Environments

Routine temperature range \( \approx 4 \text{ K} - 1600^\circ \text{C} \)

- Cryostream \( \text{N}_2 \) gas blower, 80 K – 500 K
- Liquid–He flow cryostat, down to \( \approx 4 \text{ K} \)
- Hot air blower, 1000\degree C
- Mirror furnace, up to \( \approx 1600\degree \text{C} \)
- Gas adsorption cell (0 – 100 Bar)
- Robotic 75 sample changer

All computer controlled and linked to scans
Sample Cryostream

Hot air blower

Translation stage (35 mm)

Spinner

Cryostream

Hot air blower

Halogen-bulb mirror furnace (1600°C)

Photo: Fero Simko

0 – 100 Bar non-corrosive gasses

Radiation damage
Axial translation to expose fresh sample to the beam.

Mythen curved 1d PSD

- Developed at the Swiss Light Source.
- Modular Si-strip photon-counting detector
- Unit = 1280 channels, 50 μm step, ≈ 4.83°, (step ≈ 0.004°)
- Read out ≈ 250 μs
- The best 1d PSD for soft and intermediate energies
- Excellent statistical quality in seconds
- Much faster than analysers

I11 Diamond

Australia

ALBA (Spain)
Mythen and multianalyser detectors
2d detectors

Perkin-Elmer medical imaging detectors (ID22, PETRA-III, APS, SLS-II, etc.), for fast PDF measurements.

Dectris pixel detectors. Photon counting with Si or CdTe semiconductor sensor; Pilatus 2M on BM01A.

Energy dispersive diffraction

\[ \lambda = 2d \sin \theta \]

Instead of fixed \( \lambda \) and varying \( 2\theta \), here we have a fixed \( 2\theta \) with varying \( \lambda \), with \( \lambda \) determined by the detector.

What sort of experiments?

- **Structural studies** – crystal structures, atomic PDF analysis, etc.
- **In-situ studies** – evolution with temperature, time, atmosphere, voltage, etc., phase changes, solid-state chemistry, gas adsorption, electrochemistry.
- **Anomalous scattering** – distinguish neighbouring elements in the Periodic Table.
- **High throughput** – many samples, varied compositions or preparation conditions, etc.
- **Quantitative analysis** – many phases, trace phases.
- **Microstructure** – detailed analysis of peak shapes.
- **Residual strain** – mapping peak positions in components.
- **Very flexible instruments!**

Very fast measurements

Self propagating combustion synthesis

Debye–Scherrer cones

Fast, 2D detector
We have ignition

Synthesis of Jacobsite $\text{Fe}_2\text{MnO}_4$

$12\text{Mn}_2\text{O}_3 + 8 \text{Fe}_2\text{O}_3 + 32 \text{Fe} + 9\text{NaClO}_4 \rightarrow 24 \text{Fe}_2\text{MnO}_4 + 9 \text{NaCl}$

8192 diffraction patterns
5 ms acquisition each

Powder pattern vs time

Phase Transition
Recrystallization
First reaction
Evolution of phases

Anomalous scattering

\[ F_{hkl} = \sum_n f_n \exp(2\pi i(hx_n + ky_n + lz_n)) \]

where \( f_n = f_0^n + f^n + i f''_n \)

- \( f_0^n = \) normal scattering form factor
- \( f^n = \) real anomalous scattering term
- \( i f''_n = \) imaginary anomalous scattering term
e.g. enhance sensitivity between Co and Fe

La_{1-x}Ho_xSi_2O_7 and La_{1-x}Eu_xSi_2O_7

Rare-earth pyrosilicates adopt various structures

Ho-doped material = monoclinic with 2 RE sites
Eu-doped material = tetragonal with 4 RE sites

How are the RE metal ions distributed?

Difficult (even with neutrons because of absorption)

Tune to La K edge (38.9246 keV $\leftrightarrow \lambda = 0.3185$ Å) to enhance contrast between RE elements via anomalous scattering

$f = f_0 + f' + if''$


Luminescent mixed rare-earth pyrosilicates

Fluorescence spectrum at La K edge

Kramers-Kronig inversion using CHOOCH
Consistency between samples

La$_{1-x}$Eu$_x$Si$_2$O$_7$  $x = 0.2$

La$_{1-x}$Ho$_x$Si$_2$O$_7$  $x = 0.1$

Refine with Topas

- Fit to three data sets simultaneously
- Partially flexible rigid body for Si$_2$O$_7$ units
- Constrain overall RE occupancies to known values

Rietveld fit simultaneously to the 3 data sets

Space group $P4_1$, $a = 6.77798(4)$ Å, $c = 24.6762(1)$ Å

Intensity (a.u)

2 theta (º)

Rietveld fit simultaneously to the 3 data sets
Preference for Eu in site 3

**PDF analysis**

Pair Distribution Function analysis allows structural information to be obtained despite a lack of translational periodicity in crystallographically-challenged materials, e.g. - glasses, - quasicrystals, - nanoparticles, nanocrystals, - disordered and heavily defective materials, - aperiodic materials, etc.

How long to count?

Variable count time to compensate for decrease in scattering power with \( \theta \) (form factors, B factors)

![Graph showing count time vs. \( \theta \)]


How long to count?

Know what you want to use the data for e.g. for crystallography count until

\[
R_{exp} = \left[ \frac{N}{\sum w_i y_{i\text{obs}}^2} \right]^{1/2} < 0.02
\]

- # 2\( \theta \) range
- 6 55–60
- 5 50–60
- 4 40–60
- 3 30–60
- 2 20–60
- 1 0–60

Limitations of synchrotron diffraction

- Access – proposal, waiting, travelling, sample shipping, limited beam time.
- Not yours – lack of control of facilities, conditions, options.
- Radiation damage for sensitive samples.
- Reproducibility of beamline setup?

Neutrons

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass $m_n$</td>
<td>$1.674,927,351(74) \times 10^{-27}$ kg</td>
</tr>
<tr>
<td>Charge</td>
<td>0</td>
</tr>
<tr>
<td>Spin</td>
<td>$\frac{1}{2}$</td>
</tr>
<tr>
<td>Magnetic moment</td>
<td>$-0.966,236,47(23) \times 10^{-26}$ J T$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$-1.041,875,63(25) \times 10^{-3}$ $\mu_B$</td>
</tr>
</tbody>
</table>

- Interacts with atomic nuclei via strong nuclear force and electromagnetically with unpaired spins.
- De Broglie relationship, $\lambda = \frac{h}{m_n v}$
  $\Rightarrow$ a neutron moving at $2200$ ms$^{-1}$ has $\lambda \approx 1.8$ Å.
- Very weakly absorbed, except by certain nuclei, $^6$Li, $^{10}$B, $^{113}$Cd, $^{155}$Gd, $^{157}$Gd, etc.

Production of neutrons

Nuclear reactor, via fission of $^{235}$U.

Spallation source, energetic particles, usually protons with kinetic energy of up to 1 GeV, bombard a heavy metal target such as Pb, Ta, Hg.

Rutherford Appleton lab spallation neutron source ISIS
Neutron nuclear scattering lengths

No fall off in scattering power with $2\theta$, e.g. for potassium

Vary with atomic nucleus, from isotope to isotope

X-ray at $\theta=0$

Sample holders for neutrons

Vanadium cans

Silica glass
Uses of neutron diffraction

- Magnetic structures.
- Refinement of light atoms, especially when heavy ones are also present in the sample.
- Hydrogen bonding (often via deuterated sample).
- Refinement of systems with disorder, non-stoichiometry, etc. because “high–2θ” (low–d-spacing) data quality.
- In–situ studies, complex sample set ups (because of penetration).

Monochromatic angle dispersive

Steady–state source, e.g. reactor or continuous spallation source.

\( \lambda \) selected by a single–bounce monochromator.

Multiple detectors scanned, or PSD.

e.g. D2B at ILL
Time of flight technique

- Uses a pulsed source (usually via spallation).
- Polychromatic beam.
- Fixed-angle detectors.
- Wavelength of each detected neutron is calculated from its time of flight $t$ from source to detector at distance $L$.
- De Broglie $\Rightarrow \lambda = \frac{h}{m_n v} = \frac{h}{m_n} \frac{t}{L}$

Thus $\lambda = \frac{h}{m_n} \frac{t}{L} = 2d \sin \theta$

$d = \frac{ht}{(2m_n L \sin \theta)}$

TOF diffractometers usually have multiple detector banks

HRPD at ISIS

Forward

90°

Backscatter
Other time of flight diffractometers

GEM ISIS

POWGEN ORNL

Si

\( d\)-spacing (Å)
Session 13: Introduction to Software/Problems and Interactive Rietveld Refinement

Prof John S.O. Evans
Durham University

Topas Academic or v6

- Useful for teaching as can input equations, see everything in file very quickly
- Powder and single crystal
- X-ray, neutron
- Constant $\lambda$, time of flight, energy dispersive
- Structural models, Pawley fitting, peak fitting
- Restraints, constraints, penalty only fitting
- Multi phase, multi histogram
- Non crystallographic applications
- Distortion Mode refinements
- Simulated Annealing for structure solution
- Magnetism
- Parametric refinements, stacking mode refinements

Acknowledgement

- Alan Coelho (Topas/Topas-Academic author)
- http://www.topas-academic.net/
- Bruker for dongles

Topas Graphics

Grid  Run
Zoom  Plot

Ta's
Software Interface

- Command file driven for flexibility/speed
- jEdit – free customisable java editor
- Interacts directly with software
- Helps with formatting

http://community.dur.ac.uk/john.evans/topas_academic/topas_main.htm
http://community.dur.ac.uk/john.evans/topas_workshop/pcg_workshop_menu.htm

jEdit interface

Topas/jEdit Demo

- Demonstration of jEdit to refine TiO$_2$ from laboratory X-ray data
- This is one of this afternoon’s tutorials
- Either use menus or use templates

Refining Parameters

```
str \cell params for an orthorhombic structure
a  7.31192
b  7.53699
c  7.69967
```
Refining Parameters – Using @

str 'cell params for an orthorhombic structure
  a @ 7.31192
  b @ 7.53699
  c @ 7.69967

Refining Parameters – Using Names

str 'cell params for an orthorhombic structure
  a lpa 7.31192
  b lpb 7.53699
  c lpc 7.69967

Refining Parameters – Using Names

str 'cell params for a cubic structure
  a lpa 10.60992
  b lpa 10.60992
  c lpa 10.60992

Fixing Parameters – Using !

str 'cell params for a cubic structure
  a !lpa 10.60992
  b !lpa 10.60992
  c !lpa 10.60992

• N.B. jEdit column editing – hold down ctrl key and type all !'s at once
Refining Parameters - Macros

| Zero_Error(  , 0) | fixed zero point |
| Zero_Error( @ , 0.013) | refine zero point |
| Zero_Error( !zero, 0) | fixed zero point |
| Zero_Error( zero, 0.013) | refined zero point |

User Defined Equations

`topas zero point correction in input file`

<table>
<thead>
<tr>
<th>prm zero</th>
<th>0.01</th>
</tr>
</thead>
<tbody>
<tr>
<td>th2_offset</td>
<td>= zero;</td>
</tr>
</tbody>
</table>

`topas zero point correction in input file`

| prm zero     | 0.01 |
| prm corr     | 0.003 |
| prm corr2    | 0.001 |
| th2_offset   | = corr2 * X^2 + corr * X + zero; |

User Defined Equations

`silly(?) example of topas equations`

| prm zero     | 0.01 |
| prm var1     | 0.003 |
| prm `date`   | 21 ‘st of April |
| th2_offset   | = zero + var1 * date; |

User Defined Equations

- Flexible system for defining your own equations
- Fully “programmable program”

- e.g. gsas vs topas:

  | zero 0.01 y      | shft -10.00 y |

- shft = 3600*height/π*radius
- \(2\theta_{\text{obs}} = 2\theta_{\text{calc}} + \text{zero} - 2*\text{shft}*\text{Cos}(\theta)\)

`topas height/zero point correction in input file`

| prm zero     | 0.01 |
| prm height   | 0.15 |
| th2_offset   | = zero - 2*height*Cos(Th)/radius; |
Simulated Annealing

- Flexible Simulated Annealing approach for complex structures:

```
'topas annealing expression in input file
val_on_continue = Val + Val * Rand(-0.1,0.1);
val_on_continue = ideal_coord + Rand(-0.1,0.1);
```

- Flexible definition of restraints, constraints, rigid bodies, etc

Topas Demonstration

- Group therapy refinement on Y$_2$O$_3$

Running Tutorial Problems – Session 14

- Rest of afternoon is hands-on practical Rietveld refinement
- Z:\licence\rieveld\rieveld_setup.bat
- Use jEdit/menus to set up input files
- You only need to launch topas once
- Initial problems relatively straightforward
- Later problems on different data types, restrained refinement, etc

Rietveld/Pawley Problems

- Tutorial 9 – TiO$_2$ Rietveld
- Tutorial 11 – TiO$_2$ Pawley
- Tutorial 12 – ZrW$_2$O$_8$ X-ray/neutron/neutron time of flight
- Tutorial 13 – Multiphase Rietveld refinement
- Tutorial 16 – Jeremy’s PbSO$_4$ data in .xye format for you to try in topas
- Gsas 2 (later) – Jeremy’s PbSO$_4$ data
- Tutorial 17 – Combined X-ray and neutron refinement (also gsa3/gsa4)
- Tutorial 29 - Quantitative Rietveld refinement
Session 16: Peak Shapes

Prof John S.O. Evans
Durham University

Information in a Powder Pattern

1. Peak positions determined by size and shape of unit cell – internal structure

2. Peak Intensities determined by where atoms sit in unit cell – internal structure

Information in a Powder Pattern

3. Peak widths determined by size/strain of crystallites - microstructure.

4. Background oscillations may contain information about short range order in material

Peak Shapes – View 1

- Peak shapes are a nuisance. For Rietveld refinement we only fit peaks to get an good agreement between $y_{obs}$ and $y_{calc}$ to give us an accurate structural model
- We’re therefore not interested in the mathematical details of the peak shape model
- Failure to fit the finest details of the peak shape (e.g. tails of the peaks) isn’t very important
Peak Shapes – View 2

- Peak shapes in a powder diffraction pattern result from a combination of instrumental effects (the optics you use) and sample effects (size/strain)
- There is a wealth of fascinating information contained in experimental peak shapes

Peak Shapes – 3 Approaches

- Empirical Peak Shapes
  - Used by most Rietveld packages
  - Whatever function fits the data is good

- Fundamental Parameters
  - Instrumental contribution to peak shape
  - Sample contribution to peak shape
  - Excellent fits with very few parameters

- Semi Empirical
  - Define instrument with empirical function
  - Convolute with sample contribution

Gaussian/Lorentzian Functions

<table>
<thead>
<tr>
<th>Profile Function</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gaussian, $G_{\text{av}}(x)$</td>
<td>$G_{\text{av}}(x) = \left( \frac{g_1}{fwhm} \right) \exp \left( -\frac{g_2 x^2}{fwhm^2} \right)$</td>
</tr>
<tr>
<td>where $g_1 = 2 \sqrt{\ln(2)/\pi}$, $g_2 = 4 \ln(2)$</td>
<td></td>
</tr>
<tr>
<td>Lorentzian, $L_{\text{av}}(x)$</td>
<td>$L_{\text{av}}(x) = \left( \frac{l_1}{fwhm} \right) \left( \frac{1+l_2 x^2}{fwhm^2} \right)$</td>
</tr>
<tr>
<td>where $l_1 = 2/\pi$, $l_2 = 4$</td>
<td></td>
</tr>
<tr>
<td>PseudoVoigt, $PV_{\text{av}}(x)$</td>
<td>$PV = \eta L_{\text{av}}(x) + (1-\eta)G_{\text{av}}(x)$</td>
</tr>
</tbody>
</table>

$x$ - position of reflection $2\theta\text{_{hkl}}$

$fwhm$ - full width at half maximum

$\eta$ - mixing parameter for composite function

Gaussian vs Lorentzian

- Lorentz sharp near maximum but has long tails away from peak
- Gauss smaller tails but rounded maximum

$PV = \eta L_{\text{av}}(x) + (1-\eta)G_{\text{av}}(x)$

$\eta$ - mixing parameter

PV mixes two functions

www.phys.unsw.edu.au/~mgb/pics/gausscauchy.gif
Gaussian, Lorentzian, Pseudo Voigt

\[ fwhm = \left( U \tan^2 \theta + V \tan \theta + W \right)^{1/2} \]

Lorentz: \[ fwhm = \frac{X}{\cos \theta} + Y \tan \theta \]

Refineable Parameters

\eta = 0.68 \text{ wRp}=17.6\%

\[ \eta = 1.36603 q - 0.47719 q^2 + 0.1116 q^3 \]

where

\[ q = \frac{\Gamma_t}{\Gamma} \]

\[ \Gamma = (\Gamma^2_a + \Gamma^2_b + \Gamma^2_c) \]

\[ \Gamma^2_a = \frac{\Gamma^4}{2} (A^2 + B^2 + C^2) \]

\[ \Gamma^2_b = \frac{\Gamma^4}{2} (B^2 + C^2 + D^2) \]

\[ \Gamma^2_c = \frac{\Gamma^4}{2} (C^2 + D^2 + E^2) \]

\[ \Gamma = \frac{1}{2} \left( \frac{\Gamma^4}{2} \right)^{1/2} \]

\[ \Gamma_t = \frac{\Gamma^4}{2} \]

\[ \Gamma_t = X \tan \theta + Y / \cos \theta \]

with \( U, V, W, X, Y, Z \) as refineable parameters.

\topas TCHZ peak shape function

\[ \text{TCHZ-Peak-Function}(pkx, 0.0000, pkv, 0.06474, pkw, 0.01020, pkx, 0.02355, pkz, 0.0000) \]
Fundamental Parameters Approach

• Peak widths depend on
  - X-ray source
  - Instrument
  - Sample

• Convolution or folding "blends" one function with another

\[ Y(2\theta) = (\text{Source} \otimes \text{Instrument}) \otimes \text{Sample} \]

(or empirical instrumental function)

\[ f(2\theta) \otimes g(2\theta) = \int f(2\theta)g(2\theta - 2\phi)d(2\phi) = \int g(2\phi)f(2\theta - 2\phi)d(2\phi) \]

Convolution Approach

\[ (\text{Source} \otimes \text{Instrument}) \otimes \text{Sample} = Y(2\theta) \]
An Instrumental Contribution

Definition of Convolution

- The process of convolution is one in which the product of two functions $f(2\theta)$ and $g(2\theta)$ is integrated over all space:

$$f(2\theta) \otimes g(2\theta) = \int_{-\infty}^{\infty} f(2\theta)g(2\theta - 2\theta')d(2\theta') = \int_{-\infty}^{\infty} g(2\theta')f(2\theta - 2\theta')d(2\theta')$$

- In simple terms, convolution can be understood as "blending" one function with another, producing a kind of very general "moving average". The convoluted function is obtained by setting down the origin of the first function in every possible position of the second, multiplying the values of both functions in each position, and taking the sum of all operations.
- See e.g. [http://www.jhu.edu/~signals/discreteconv/](http://www.jhu.edu/~signals/discreteconv/)

Joy of Convolution

- Web demo
  2. [http://www.jhu.edu/~signals/convolve/index.html](http://www.jhu.edu/~signals/convolve/index.html)
  3. [http://www.jhu.edu/~signals/discreteconv/](http://www.jhu.edu/~signals/discreteconv/)

Sample Contributions - Size

$$\beta = k \lambda / L_{Vol} \cos \theta$$

- Scherrer formula
- $\beta$ full width half maximum; $k$ a constant
- $L_{Vol}$ is volume weighted mean column height; only for cubic crystals and h00 reflections is it equal to $L_0$ in figures below
Size Distribution

- Make sure you're measuring the same thing

Monodispersed spheres $L_{\text{Vol}} = 1.5 \times \text{radius}$

Average size - beware

Particle Size Broadening

Sample Contributions - Strain

$$\beta = 4\varepsilon_0 \tan \theta$$

- $d$-spacings of $d+\Delta d$ and $d-\Delta d$
- $\varepsilon_0 = \Delta d/d$
- Assume Bragg's law gives different $2\theta$ for different $d$-spacings
Sample Contributions - Strain

No strain
Macrostrain – homogenous strain
Microstrain – inhomogenous strain
Microstrain and macrostrain

X-ray Particle Size from Peak Shape

- Size broadening – "broad over whole 2-theta range"
- Strain broadening – "narrow at low 2-theta"

High vs Medium Resolution

Large vs Small Domains
Joy of Convolution

- Topas Demo
- File: conv_joy_01.inp

Sample Contributions - Caveat

- Be careful!
- See links in tutorial
  - http://community.dur.ac.uk/john.evans/topas_workshop/size_strain.htm

Source Profile

N.B. source profile only much sharper than observed peak

Source \( \times \) Equatorial

N.B. peak now considerably broadened by instrument
Source ★ Equatorial ★ Axial

N.B. peak now has asymmetry

Source ★ Equatorial ★ Axial ★ Sample

N.B. peak maximum not at calculated 2θ

Topas Language

```
Radius(217) 'diffractometer radius
Divergence(1) 'divergence slit deg
axial_conv
    filament_length  12
    sample_length 15
    receiving_slit_length 12
    primary_soller_angle 5.1
    secondary_soller_angle 5
Slit_Width(0.1) 'receiving slit
CS_L(size_lor, 329.49186) 'size term nm
Strain_G(strain_g, 0.04939) 'strain term
```

Peak cut off

GSAS: W 0.1
Clare’s Cu₂WS₄ – hkl dependent fwhm

- fwhm vs 2θ may reveal odd things
- 2 phases? Anisotropic peak broadening?

**Tutorial 19 (hard!)**

- Take an experimental data set
- Determine fwhm for all peaks and plot in excel
- Use excel to fit fwhm=f(2θ) functions
  - fwhm = U tan²θ + V tanθ + W
  - fwhm = U 2θ² + V 2θ + W
- Try these same functions in a Rietveld refinement in topas
- Try a fundamental parameters approach in topas and get a better fit with fewer parameters.

**hkl-dependent peak shapes**

- Relatively common to find peaks have width (or asymmetry) that is hkl-dependent
  \[ \text{fwhm} = d^2 \sqrt{s 400 \times h^4 + s 040 \times k^4 + s 004 \times l^4 + … + s 112 \times h \times k \times l^2 \tan \theta} \]
- Consider convoluting an additional hkl-dependent function onto peak shape (e.g. a spherical harmonic function)
- Consider more exotic empirical convolutions (e.g. for clays)
- Consider a “stacking fault” or “diffax like” Rietveld refinement

**Tutorials**

- See:
  - tutorial 18 – playing with convolutions
  - tutorial 20 – fundamental parameters fitting
  - tutorial 21 - Size/Strain Analysis: Shows how size/strain can be determined in topas using the CeO₂ round robin data and an empirical instrumental function
  - tutorial 22 – determining the size of nanoparticles
Session 17: Restraints, Constraints, Rigid Bodies and Structure Solution

Prof John S.O. Evans
Durham University

Data Compression

3D Information Compressed onto 1D

‘...data compressed into one dimension...’

Insufficient Information

- Powder pattern 3D diffraction data compressed onto 1D
- Loss of “information” relative to a single crystal experiment
- Single crystal people like 10 observations (10 hkl reflections) per refined parameter
- How many “observations” do we have in a powder pattern?
Peak Overlap/Resolution $\Delta d/d$ (%)

```
0.36 %  0.12 %  0.04 %  0.0 %
```

alvo4_tch.inp

- 5–80 0.02 step 3750 observations
- 530 hkl reflections in 2θ range

```
STR($P_{-1}$, AlVO4)

a @ 6.54138'
b @ 7.75971'
c @ 9.13591'
al @ 96.18561'
be @ 107.23757'
ga @ 101.40086'
```

How Many Peaks?

```
Counts
0 1,000 2,000 3,000 4,000 5,000 6,000 7,000 8,000 9,000 10,000
```

Al VO4 100.00 %
How Many Peaks?

Reflection Density and Peak Overlap

Quantifying

Information in a Powder Pattern

- How much information is there in a powder pattern?
- Rarely enough

See literature by e.g. Giacovazzo/David/Di Sivia
Restraints

- Remember our Straight Line fitting problem
- Line must pass through (0, 0)

\[
\begin{pmatrix}
1 & 2 & 3 & 4 & 0 \\
1 & 1 & 1 & 1 & 1
\end{pmatrix} = \begin{pmatrix}
m \\
c
\end{pmatrix} = \begin{pmatrix}
1 & 2 & 3 & 4 & 0 \\
1 & 1 & 1 & 1 & 1
\end{pmatrix} \begin{pmatrix}
2 \\
5 \\
10 \\
18 \\
0
\end{pmatrix}
\]

\[m = 4.4 \quad c = -1.8\]

Extra information as an observation

\[
\begin{pmatrix}
1 & 2 & 3 & 4 & 0 \\
1 & 1 & 1 & 1 & 1
\end{pmatrix} = \begin{pmatrix}
m \\
c
\end{pmatrix} = \begin{pmatrix}
1 & 2 & 3 & 4 & 0 \\
1 & 1 & 1 & 1 & 1
\end{pmatrix} \begin{pmatrix}
2 \\
5 \\
10 \\
18 \\
0
\end{pmatrix}
\]

\[m = 3.81 \quad c = -0.03\]

Higher weight

Restraints

- Bring in chemical information
- Dealt with in least squares in the same way as data
- “Soft Restraints”

\[
\chi^2_{\text{data}} = \left(\frac{R_{\text{wp}}}{R_{\text{exp}}}\right)^2
\]

\[
\chi^2_{\text{tot}} = K_1 \chi^2_{\text{data}} + K_2 \chi^2_{\text{rest}}
\]

Topas Bond Lengths/Angles

- You might know that Zr1-O2 distance should be ~2.075 Å
- Apply a “penalty” if it’s not that value
- Penalty = (value-2.075)^2

Distance_Restrain(Zr1 O1, #ideal_dist, #actual dist, #tolerance, #weight)

Distance_Restrain(Zr1 O1, 2.075, 2.037, 0.01, 1)

Angle_Restrain(O1 Zr2 O2, 90, 91, 1, 1)

Penalty = weight * (2.075-2.037)^2;
Restraints

• See tutorials

Constraints

• Force sub-sections of structure to be rigid
• Dealt with in least squares in the same way as symmetry
• “Hard Constraints”

Constraints

• Remember our straight line that had to pass through the origin:

\[ m \times x + c = y \]

\[
\begin{pmatrix}
1 & 2 & 3 & 4 & 1 & 1 \\
1 & 1 & 1 & 1 & 3 & 1 \\
4 & 1 & 1 & 1 & 1 & 10 \\
\end{pmatrix}
\begin{pmatrix}
m \\
c \\
\end{pmatrix}
= \begin{pmatrix}
2 \\
5 \\
10 \\
18 \\
\end{pmatrix}
\]

\[ m = 4.4 \]
\[ c = -1.8 \]

Constraints/Rigid Bodies

• e.g. force the Zr1-O2 bond to be exactly 2.075 Å
• e.g. rigid body
• How many parameters?

\textbf{macro} Octahedra\( (\text{Zr1, o1, o2, o3, o4, o5, o6, 2.075}) \)
{
Point_for_site(s0, 0, 0, 0)
Point_for_site(s1, r, 0, 0)
Point_for_site(s2, -r, 0, 0)
Point_for_site(s3, 0, r, 0)
Point_for_site(s4, 0, -r, 0)
Point_for_site(s5, 0, 0, r)
Point_for_site(s6, 0, 0, -r)
}
**TLS Matrices**

- Atoms on both sides of a rigid group ought to vibrate in related ways
- Atoms/adps independently – how many parameters?
- Rigid body/TLS e.g. 8 parameters

**Rigid Bodies**

- P$_2$O$_7$ groups are well understood – 2 parameters per P$_2$O$_7$?

**Z-Matrix**

- Use distance and angle “road map” to describe coordinates

**Rigid Bodies**

- Define in terms of rigid hexagons for benzene rings
- Allow a torsion angle for rings
- Allow a torsion angle for NMe$_2$ groups and CO$_2$H group
Z-matrix – See tutorials

The following sections define molecules using rigid bodies

rigid
load z_matrix {
  C1a
  C4a C1a c1c4 2.14429'
  C2a C1a c1c2 1.53603' C4a c1c2c4 79.2492'
  C5a C4a =c1c2; C1a =c1c2c4; C2a c2c1c4 247.2488'
  C3a C4a =c1c2; C1a =c1c2c4; C2a 0
  C6a C1a =c1c2; C4a =c1c2c4; C2a =360-c2c1c4c5;
  O1a C1a clx 1.44771' C4a = Rad*ArcCos(0.5*c1c4/c1x); C5a =c2c1c4c5/2.;
  H1a C1a tch 0.951 O1a xclh1 246.3615' C4a 0
  H6a C4a =chj; O1a =xclh1; C1a 0
  H2a C2a =chj; C1a c1c2hex 110.8450' O1a xclc2hex 276.4742'
  H7a C5a =chj; C4a =c1c2hex; O1a =xclc2hex;
  H9a C6a =chj; C1a c1c2hex; O1a =360-xclc2hex;
  H4a C3a =chj; C4a =c1c2hex; O1a =360-xclc2hex;
  H3a C2a =chj; C1a c1c2hex 113.9087' O1a xclc2hex 157.0197'
  H8a C5a =chj; C4a =c1c2hex; O1a =xclc2hex;
  H5a C3a =chj; C4a =c1c2hex; O1a =360-xclc2hex;
  H10a C6a =chj; C1a =c1c2hex; O1a =360-xclc2hex;
}

Rotate about axes (xrota -306.46415', yrota 119.57678', zrota -131.40232')
Translate (xtransa 0.84783', ytransa 0.64916', ztransa 0.78382')

Tutorials – Restraints/Constraints

- Tutorial 12 – ZrW₂O₈
- Tutorial 23 – refining an organic using restraints then as a rigid group
- Tutorial 24 - organic molecules from synchrotron data using z-matrix formalism
- GSAS 4 – restraints/combined refinement oxide
- GSAS 5 – Rigid bodies Sc₂(WO₄)₃ using TLS matrices
- GSAS 7 – organic using restraints
- GSAS 9 – Ni coordination polymer using restraints

Session 18: Introduction to GSAS/Fullprof

Prof John S.O. Evans
Durham University

UK #1 for economic and societal impact of chemistry research

GSAS and GSAS-II

- General Structural Analysis System
- Bob Von Dreele/Alan Larson
- Very widely used
- Magnetic refinements
- Run via expedt/expgui (Brian Toby)
- Actually has a .exp file (like .inp file) in background

- GSAS-II new version
- Open source python
- Constantly updated
GSAS files

- .EXP contains all info for refinement
  - could edit directly but fixed format
  - expgui is in some ways a “text editor” like jEdit in that it just modifies the .exp file
- .LST contains all results from each cycle
- .P01, .P02 are data in gsas internal format (produced by powpref)
- .INST are instrument parameter files describing experimental set up
  - .00a, .00b, .016, etc are (endless) backup .EXP files produced on running gsas

GSAS .exp file

CRS1 PNAM y2o3

CRS1 NATOM 3

GSAS .inst instrument parameter file

- Describes the instrument you’re using
- Just like parts of the .inp file

add_dO_C451.RAM

start_X 0 finish_X 180
d0500 Bruker D8 Advance diffractometer Cu Ka1/2 2 line emission
LP_Factor(1/8h monochromator, 26.4)
CuKa1(0.0001)
CuKa2(0.0001)
Zero_Error(zero,-0.03261`)TCHZ_Peak_TYPE(pku, 0.07492`, pkv, -0.09325`, pkw, 0.02611`, !pkz, 0.0000,pky, 0.13421`, !pkxz, 0.0000)

GSAS .exp file (cont)

Phase information

Scattering factors, size, etc

Statistics
### GSAS .inst file – LP Correction

<table>
<thead>
<tr>
<th>LP_Factor(1th2_monochromator, 26.6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuKα2 (0.0001)</td>
</tr>
</tbody>
</table>

| INS 1 ICONS 1.5406 1.5444 0.0000 0.555 0 0.500 |

**Topas:** $2\theta_m=26.6$

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

**GSAS:** IPOL = 0, $Ph(POLA) = 0.555$

$$\frac{Ph \times (1-P) \cos^2 2\theta}{2 \sin \theta \cos \theta}$$

$$LP_{\_Factor} = \frac{1 + \cos^2 2\theta \times 0.8}{\cos \theta \sin \theta} \quad \frac{0.5 + \cos^2 2\theta \times 0.4}{2 \cos \theta \sin \theta} = \left(\frac{0.555 + 0.444 \cos^2 2\theta}{2 \cos \theta \sin \theta}\right)$$

**GSAS:** IPOL = 1, $Ph(POLA) = 0.800$

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

$$LP_{\_Factor} = \frac{1 + \cos^2 2\theta \times 0.8}{\cos \theta \sin \theta} \quad \frac{0.5 + \cos^2 2\theta \times 0.4}{2 \cos \theta \sin \theta} = \left(\frac{0.555 + 0.444 \cos^2 2\theta}{2 \cos \theta \sin \theta}\right)$$

### Mistakes

- Hardest thing in practice is spotting mistakes
- You don’t know what the “right” answer is
- Are there errors in model or data?
- Ivana’s “Rietveld Crimes”

- mistake_02 to mistake_08 contain data with “errors” in them – solve the errors and win a prize!
- Stick to isotropic temperature factors
- Stick to a TCHz analytical peak shape function
- For these instruments you can fix pkx and pkz at 0
Understanding Things

- Look in topas.log
- Look in topas.inc
- Make your own local.inc

Other Things

- Distortion Mode refinements (Tutorial 36-38)
  - using group theory to help with phase transitions
- Quantitative Rietveld (Tutorial 29)
  - Using Nikki Scarlett/Ian Madsen’s Round Robin data
- Size strain analysis (Tutorial 30)
  - Using Round robin data
- Single crystal data (Tutorial 32/33)
- Parametric/Surface Fitting (Tutorial 34/35)

Checklist: Start to Finish

- Go through a problem or tutorials taking you through the whole process of data analysis
  - Fit peaks (Tutorial 6)
  - Index (manually or in topas) (Tutorial 7)
  - Work out spacegroup (Session 1/2)
  - Pawley/Le Bail fit for indication of fit quality possible (Tutorial 4)
  - Structure solution? (Tutorial 26/27/28)
  - Rietveld refinement (Tutorial 9 etc)
- e.g. the PbSO₄ data in Tutorial 16

Checklist: Key Skills

- Data types
  - Lab xrd
  - Synchrotron xrd
  - Neutron constant wavelength
  - Neutron time of flight
- Sample types
  - Inorganic extended structures
  - Small molecule structures
- Software Y₂O₃ in
  - Topas
  - GSAS
  - Fullprof
- Multiphase refinement
- Multiple dataset refinement
Checklist: Happy?

• Are you leaving knowing what you hoped you’d learn?

• If not ask!

• PLEASE COMPLETE POST-COURSE QUESTIONNAIRE
<table>
<thead>
<tr>
<th></th>
<th>C₄, S₄</th>
<th>C₄h, D₄h, C₄v, D₄h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexagonal</td>
<td>C₆, C₃h</td>
<td>C₆h, D₆h, C₆v, D₆h</td>
</tr>
<tr>
<td>Trigonal</td>
<td>C₃, C₃i</td>
<td>D₃, C₃v, D₃d</td>
</tr>
<tr>
<td>Cubic</td>
<td>T</td>
<td>Tᵥ, T₄, O, O₄h</td>
</tr>
</tbody>
</table>

1.2 Appendix: International Tables for Crystallography

The International Tables for Crystallography, Volume A, Space-group symmetry, (http://dx.doi.org/10.1107/97809553602060000100) list symmetry properties of the 230 space groups used for analysis and description of crystal structures. The symmetry information is presented symbolically, graphically and mathematically. As an example, information given on the pages for the space group Pnma is explained in this Appendix.

International tables contain a minimum of two pages for each space group. The first of these two pages for space group Pnma is shown in Figure 1.62. The upper line of text contains the space-group symbol Pnma, the symbols of the point group using Schönflies (D₂h) and Hermann–Maugin (mmm) notations and the crystal system (Orthorhombic). The next line gives the number (62) of the space group (from 1 to 230; in order of ascending symmetry), the full space-group symbol (P 2₁/m 2₁/m 2₁/a), and the symbol for the Patterson symmetry (Pmmm); the latter is the symmetry for a special type of electron-density map useful for determining crystal structures. The symmetry elements given in the full space-group symbol are oriented relative to the directions given in Table 1.3.

The space-group diagram is given below these lines, and shows the location of the symmetry elements in space. For an orthorhombic space group, the figure in the top left is the projection of the unit cell with the a axis down the projection plane (page), b horizontal, and the origin in the upper left hand corner. The other two orthographic projections of the unit cell are drawn to the right and below. The label along the edge of each of the three projections gives the full space-group symbol as if that edge were the unit-cell parameter b in the ab plane of the paper. Only the top left symbol is the symbol of the group in standard orientation. For all groups except cubic, a corresponding point diagram is drawn (bottom right in Figure 1.62), showing how a general point x,y,z represented by “O” is repeated by the symmetry elements. The sign of the z coordinate is given, and a “½+” means ½ + z. We can therefore consider ourselves as looking down on top of the unit cell, with one of the coordinates being the height above the base of the cell. Where the circle contains a dash, it has a change in handedness relative to the original site.

The positions in the point diagram can be easily generated if one knows the symbols for symmetry elements. If we focus initially on the top left figure, the n, m and a mirror (glide) planes in the space-group symbol are represented by the dashed dotted line ..., the full line — and the ■ symbol, respectively. The arrow on the a glide symbol represents the direction of translation. The a glide plane is at a height of z = ½. In the other projections shown, these same symmetry elements are drawn with different symbols. In the diagram on the top right (ac plane, origin top right, c down, a across) the mirror plane is now ¼ above the plane and is shown as ■. In the lower left (bc plane,
origin bottom left, b across, c up) the n glide is shown as . The ... symbol in this figure is the original a glide viewed side on (note that the direction of translation is now out of the page). The inversion centers, –1, are marked with small circles *, the twofold screw axes 2, have symbol . If this symbol has a circle in its centre, it means a 2, with a perpendicular m (2/m; it generates a centre of inversion at the crossing). If the 2, axis is parallel to the projection plane, the symbol used is a half-arrow →.

**Origin** (in this case listed as –1 on 1 2, 1) defines the placement of the origin with respect to the symmetry elements. By convention, the origin is placed at an inversion where possible. In some space groups, different origins can be chosen or some of the origin coordinates may be undefined (a “free” or “floating” origin).

**Asymmetric unit**, here 0 ≤ x ≤ 1/2; 0 ≤ y ≤ 1/2; 0 ≤ z ≤ 1, defines the smallest unit from which application of all symmetry operations of the space group fills the space, thus creating the structure.

**Symmetry operations** contains a numbered list of the symmetry elements and their placements. Here the list contains: (1) the identity; (2), (3) and (4) the 2, axes; (5) the inversion located at the origin (0,0,0); (6) the a glide in the xy plane at z = 1/4; (7) the mirror m in the xz plane at y = 1/4; and (8) the n glide in the yz plane at x = 1/4. For operations (2), (3), (4) and (8), non-lattice translations are specified in round brackets. This tells us that (2) to (4) are actually 2, screw axes rather than two-fold rotation axes.

The second page for space group *Pnma* (Figure 1.63) begins with **Generators selected**. This lists the symmetry operations required to generate all the symmetry elements and always contains the identity operation numbered (1) and the three translations corresponding to the three basis vectors a, b and c: t(1, 0, 0), t(0, 1, 0) and t(0, 0, 1). For non-primitive space groups, centering translations would come next. The remaining generators of the space group are identified by the numbering used in the **Symmetry operations**; in this particular case, the symmetry operations are (2), (3) and (5).

Under the heading **Positions** there are several subheadings. **Multiplicity** expresses how many times a given position is repeated in the cell upon action of the symmetry operations. The highest multiplicity is characteristic of a general position (a point that does not lie on any symmetry element, except identity). This general position has multiplicity 8 for *Pnma*. This means that if you place an atom at an arbitrary point x,y,z in this space group, seven other symmetry-equivalent atomic sites will be generated. The general position is followed by special positions, here all have multiplicity 4. These have
coordinates that lie on one or more of the symmetry elements, the symmetry operations of which project the atom on itself, decreasing the multiplicity.

The Wyckoff letter is an alphabetical label given to atomic (Wyckoff) positions that starts with an “a” for one of the lowest-multiplicity sites at the bottom. The Site symmetry gives the point symmetry for the site. The Coordinates show how the original atomic coordinates \( x,y,z \) are transformed after the symmetry operations have been performed (eight such operations in Figure 1.62), and the number of resulting coordinates is an integer fraction of the original. Reflection conditions are conditions for the appearance of \( hkl \) Bragg reflections when atoms are placed in the given Wyckoff positions. In a structure where atoms occupy only this Wyckoff site, Bragg reflections that do not fulfill these conditions are extinct.

If we skip the Symmetry of special projections entry (it involves plane groups which we won’t use in this text), the rest of the information concerns relations between subgroups and supergroups. The order of a group is the number of symmetry operations it contains and corresponds to the multiplicity of the general point \( x,y,z \). A group \( S \) is called a (proper) subgroup to the group \( G \) if all symmetry elements of \( S \) are also present in \( G \) and the order of \( G \) divided by the order of \( S \) is an integer. Knowledge of group–subgroup relationships gives a clue on how a gradual removal of symmetry elements via deformations or via ordering of atoms, charges or magnetic moments changes a parent structure into the less symmetrical structure of a subgroup. As we shall see in Chapter 4, these considerations may eventually be used to investigate structural phase transitions.

The Maximal non-isomorphic subgroups are those closest to the parent group. There is no other group in the hierarchy between the group and its maximal subgroup. According to whether the group-to-subgroup transition involves the loss of rotational or translational symmetry elements, two types of maximal non-isomorphic subgroups are distinguished: Translationengleiche subgroups (under heading I) are those that arise by decreasing the amount of rotational symmetry operations. Klassengleiche subgroups are those that emerge when only translational symmetry is decreased. Those klassengleiche subgroups that retain the same conventional cell are listed under IIa; and this obviously is only possible by removal of centering. Those klassengleiche subgroups that acquire a larger conventional cell than the parent group are listed under IIb. For \( Pnma \) only type I subgroups exist and if we lose symmetry elements (5) to (8), the space-group symmetry is lowered to \( P2_12_12_1 \), whereas if we lose symmetry elements (2), (4), (5) and (7) the space-group symmetry becomes \( Pn2_1a \).

The category IIc lists the Maximal isomorphic subgroups of the lowest index, where the term isomorphic indicates that the space group remains the same (only the unit cell increases). Since the number of possible enlargements is infinite, the condition of lowest index is applied. The index is an integer ratio between the number of symmetry elements in a group and its subgroup, and the condition ensures that only “nearest” subgroups are listed. The index is specified in a square bracket in the listing. Minimal non-isomorphic supergroups are the last group listed on the page. These relate to the situation in which the present group is a subgroup of a supergroup and let one investigate higher possible symmetries. The subdivisions into the translationengleiche types I and the klassengleiche types II have the same meaning as explained above.

1.3 Appendix: Nomenclature of silicates

A systematic nomenclature of silicate anions has been developed by Friedrich Liebau. The newest version [20] places the formula of the silicate anion in a square bracket and all geometry information is given in a preceding curly bracket, as \{\text{Si}_4\text{O}_{12}\}^{	ext{2-}}. In this scheme, \( B \) stands for branchedness of the silicate anion, \( P \) for the periodicity of the tetrahedral chain, \( M \) for multiplicity and \( D \) for dimensionality. The branchedness parameter \( B \) describes branching along a chain or ring: \( uB \) stands for unbranched, \( oB \) open branched, \( IB \) loop branched. The multiplicity parameter \( M \) describes how many parallel strings of tetrahedra the chain has. As an example, the tremolite chain in Figure 1.58 is a double chain. The dimensionality parameter \( D \) of the silicate anion is a “1” for a terminated anion, \( r \) for ring, \( \frac{1}{4} \) for infinite chain, \( \frac{2}{4} \) for a layer, \( \frac{3}{4} \) for a framework. The periodicity of the chain \( P \) is the number of tetrahedra in the repeat unit along the chain direction (along the ring for ring chains), excluding any branches. When a name is
Rietveld refinement guidelines

L. B. MCCUSKER, R. B. VON DREELE, D. E. COX, L. LOUER and P. SCARDI

Laboratorium für Kristallographie, ETH, Zürich, Switzerland, 2 LANSE, Los Alamos National Laboratory, Los Alamos, NM, USA, 3 Physics Department, Brookhaven National Laboratory, Brookhaven, NY, USA, 4 Laboratoire de Chimie des Solides et Inorganique Moléculaire (UMR 6511 CNRS), Université de Rennes I, Rennes, France, and 5 Dipartimento di Ingegneria dei Materiali, Università di Trento, 38050 Mesiano (TN), Italy.

E-mail: lynn.mccusker@kristall.ee.eth.ch

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Abstract

A set of general guidelines for structure refinement using the Rietveld (whole-profile) method has been formulated by the International Union of Crystallography Commission on Powder Diffraction. The practical rather than the theoretical aspects of each step in a typical Rietveld refinement are discussed with a view to guiding newcomers in the field. The focus is on X-ray powder diffraction data collected on a laboratory instrument, but features specific to data from neutron (both constant-wavelength and time-of-flight) and synchrotron radiation sources are also addressed. The topics covered include (i) data collection, (ii) background correction, (iii) peak-shape function, (iv) refinement of profile parameters, (v) Fourier analysis with powder diffraction data, (vi) refinement of structural parameters, (vii) use of geometric restraints, and an overview of e.s.d.'s. The interpretation of R-values and (x) some common problems and possible solutions.

1. Introduction

The results of two Rietveld refinement (Rietveld, 1969) studies of powder diffraction data were presented at the International Conference on Crystallography held in Paris in 1974 by Hill & Cranswick and by Bragg-Brentano and transmission (Debye-Scherer, Guinier) geometries are considered. Features that are specific to data from neutron (constant-wavelength and/or time-of-flight) and synchrotron (or parallel-beam laboratory) sources are addressed separately where appropriate. While the use of Rietveld refinement for quantitative analysis is not dealt with specifically, the guidelines are also valid for this application. However, for additional information on this topic, the reader is referred to the paper by Hill (1991).

In the following sections, the practical aspects of each step of a typical Rietveld refinement (including some of the critical factors in the data collection itself) are discussed, in the hope that the rapidly growing powder diffraction community can benefit from a relatively concise presentation of the pitfalls awaiting them and of some of the possible solutions. Each topic is handled separately to enable easy reference. A newcomer to Rietveld refinement is encouraged to start with the refinement of the structure of a standard material such as ZrO₂ (Hill & Cranswick, 1994) and to compare the results with the published ones. For more detailed information, the reader is referred to The Rietveld Method edited by R. A. Young (1993) and the monograph Modern Powder Diffraction edited by Bish & Post (1989). Guidelines for the publication of the results of Rietveld analyses can be found in the paper by Young (1982).

It has been assumed that the Rietveld refinement software used is reliable. For an up-to-date list of Rietveld refinement programs, see the CPD WWW pages (current location: http://www.iucr.org/cpd-top/comm/ cpd). Should the WWW site change, the link from the IUCR site (http://www.iucr.org) will be modified accordingly.

2. Data collection

For a Rietveld refinement, it is essential that the powder diffraction data be collected appropriately. Factors to consider prior to data collection are the geometry of the diffractometer, the quality of the instrument alignment and calibration, the most suitable radiation (e.g. conventional or Cu Kα; synchrotron X-ray or neutron), the wavelength, appropriate sample preparation and thickness, slit sizes, and necessary counting time. If the relative intensities of the peaks and/or the 2θ spacings are not correct, no amount of time spent on the structure refinement will yield sensible results. It is not the purpose of this paper to delve into the intricacies of data collection, but it is perhaps appropriate to indicate briefly where common errors occur.

For Bragg-Brentano geometries, it is important that the incident beam be kept on the sample at all angles to ensure a constant-volume condition. Quite often, the divergence slits used are too wide and the beam hits the sample holder at low angles, so the intensities measured at these angles are too low. Some programs can correct for this, but most do not. If a correction is used, the shape of the sample holder (i.e. circular or rectangular) must also be taken into account. It should not be assumed that using a rotating circular sample will eliminate the problem. For efficient data collection, smaller slits can be used at low angles and wider ones at higher angles, provided that the different ranges are appropriately scaled to one another and the e.s.d.'s are correctly calculated. Alternatively, each section can be treated as a separate data-set in a multi-data-set Rietveld refinement. The latter approach also eliminates any problems caused by different resolution characteristics in the different sections.

Many laboratory diffractometers are equipped with automatic divergence slits, which open as a function of 2θ. While there is a substantial gain in diffraction intensity at high angles with such slits, there is also a progressive deterioration of the parafocusing condition and therefore of the resolution as 2θ increases. In Bragg-Brentano geometry, the flat specimen surface is tangent to the parafocusing circle as 2θ increases, so a large part of this circle diminishes at the same time. The illuminated area of the sample is reduced, so the flat- scan pattern is also a function of 2θ. Despite the size of the divergence circle. Furthermore, if the varying slit widths are used, a progressive angular-dependent defocusing occurs, which affects the quality of the data detected. Although major problems can be avoided by using slits which are too small to be used in the 2θ range of interest, the data quality decreases as 2θ increases. Therefore, the use of such slits for a Rietveld refinement is not recommended.

To ensure good counting statistics throughout an X-ray powder diffraction pattern, more time should be spent on data collection at high angles where the diffracted intensity is lower. An appropriate data-collection strategy will depend on the nature of the sample (e.g. whether it is powdery or complex). However, it is generally not more than ten) across the top of each peak to minimize the time spent on the background and to ensure that the 2θ scale is correct (at half-maximum), the time per step should approximately compensate for the gradual decline in intensity with 2θ (Madsen & Hill, 1991; 64, 80, 96). If the maximum value is chosen to give the most useful data (i.e. as high as possible). Care must be taken that the e.s.d.'s are properly calculated for different counting times.

Another problem is that of sample transparency. The assumption for reflection geometry is that the sample is infinitely thick (i.e. the X-ray beam is totally absorbed by the sample). If the sample contains only light elements, this condition might not be fulfilled. Then the constant-volume assumption is not valid and the intensities measured at high angles will be too low unless an appropriate correction is introduced at the refinement stage. For such materials, transmission geometry is usually to be preferred.

On the other hand, heavily absorbing samples can be a problem in a transmission set-up, because the incident beam cannot penetrate the whole sample. In this case, the sample may have to be divided with a light-element material (e.g. diamond powder or glass beads). For such samples, reflection geometry is preferred. However, for highly absorbing materials, a potential source of error in reflection geometry is that of surface roughness. This can reduce the intensity of low-angle reflections and lead to anomalously low thermal parameters in refinement. Corrections have been suggested by Sauter (1972), Masciocchi et al. (1991) and Potchke et al. (1993), and have been implemented in some programs.

Preferred-orientation effects can be difficult to eliminate, especially for flat-plate specimens (even when back or side loaded), and these can also lead to incorrect intensity measurements. If the intensities show a strong hkl dependence (e.g. all 00l reflections are strong and all h00 weak), preferred orientation of the crystals should be suspected. Masciocchi et al. (1995) have developed methods for analyzing powder diffraction data for preferred-orientation effects. However, if the preferred orientation is not strong, or if the data are very noisy, it may be possible to detect the presence of preferred-orientation effects. Further work is required to find effective methods for dealing with these problems. However, the problem can be alleviated by using a weaker incident beam, which will tend to reduce the intensity of low-angle reflections and lead to anomalously low thermal parameters in refinement. If the sample is transparent, the problem will be reduced. If the sample is opaque, the problem will be increased.

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dictate that a flat-plate sample be used, spray drying the sample to minimize preferred orientation should be considered. Rotation of a flat-plate sample in its own plane and within its orientation Effects.

An ideal particle size within a powder sample is circa 1-5 μm. If large crystallites are used, there are fewer crystallites per unit volume (e.g. not all crystallite orientations are equally represented) may become a problem. This can cause nonuniform macromolecular structure. The reason that, unlike preferred orientation effects, cannot be corrected at the refinement stage. Sample rotation will improve the particle statistics and is strongly recommended. If smaller particles are used, line-broadening effects due to crystallite size begin to become apparent. If there are one or more large crystallites within a sample of smaller ones (‘rocks in the dust’), the relative intensities of the reflections originating from the larger crystallites will be too high in comparison with the other reflections and as with nonrandomness, no correction can be applied at the refinement stage. For more information on sample preparation, see Bish & Reynolds (1989) or Buhurke et al. (1998).

The 20 values should be carefully calibrated using several peaks from a standard material (e.g. NIST Si standard SrRM 640b and/or fluorophlogopite mica SRM 675 for low angles). Almost all diffractometers can be adjusted so that the deviations of the measured peak positions from the correct ones are less than 0.01° (2θ). Furthermore, the diffractometer should be set-up to give a low background and maximum peak resolution (small peak widths) if a complex pattern with significant reflection overlap is to be measured (e.g. small receiving slits, pre-detector Soller slits if available, receiving slit on the focusing circle, 0.3 mm capillary or smaller for transmission geometry, monochromatic radiation (e.g. Cu Ka, rather than Cu Kα2, if possible). Although longer data-acquisition times are required with monochromatic radiation, particularly advantageous are the higher number of counts in the pattern is halved (so the severe overlap of reflections begins at higher angles) and therefore the background is lower. If both αs and θs components are used in the data collection, the spectral distribution (intensity ratios) and dispersion (profile changes as a function of 2θ). Any attempt to smooth the diffraction data before doing a Rietveld refinement must be resisted. Significant contributions to the background and useful information will be lost. Smoothing beyond point correlations (off-diagonal weight matrix elements) which will give falsely lower e.d.f.s in the refinement. For more information on data-collection aspects, the reader is referred to the results of the second round robin (Hill & Cawthorn, 1994), to the review on powder diffraction by Langford & Louër (1996) and to the monograph edited by Bish & Post (1989) mentioned earlier. For information regarding the effect of systematic errors on powder diffraction data see Wilson (1963).

Synchrotron. There are a number of options for data collection at a synchrotron facility, which may not be familiar to users of conventional laboratory equipment. Typically, only a fraction of the discussion is included in this chapter. There are two main beamline scientist prior to starting an experiment. These options involve a compromise between resolution, intensity and time available. It is often most helpful to consider the synchrotron X-ray experiments and data collected in this way (especially at shorter wavelengths) generally seem to give the most satisfactory refinements. Anomalous (resonant) scattering techniques can be used to enhance the contrast between elements close to one another in the Periodic Table and thereby serve as a probe of cation distribution (or even oxidation states in some cases). If the K or Lα edge is accessible at the beamline, it is recommended that for such experiments at least two data-sets be collected: one about 10–20 eV below the absorption edge (where the scattering factor may be reduced by 5–20 electrons depending on the atomic number) and one at least 1 keV below the edge, or, if feasible, well above the edge. Because a synchrotron beam decays with time, the incident-beam intensity must be monitored during an experiment (resulting data normalized for this decay) Data can be collected with constant monitor counts (variable time) or constant time (variable monitor counts) per step. In the latter case, the measured intensity must be normalized using the monitor counts and the e.s.d’s calculated accordingly. A word of warning: not all programs can accommodate the input of e.s.d’s. If this is the case, constant monitor counts should be used to collect the data. Otherwise, the weighting scheme used in refinement will be incorrect. The value of the polarization factor of the incident beam is another quantity which will be needed in the subsequent data processing. The wavelength down to 0.4 Å should be as close as possible to zero. This is because neutrons are scattered by the atomic nuclei, the only one-off in intensity as a function of scattering angle is due to the thermal motion of the atoms. Consequently, the scattered intensity at high angles is only slightly lower that at low angles and therefore wavelength cannot be gained by variable-speed data collections as suggested above for X-ray diffraction experiments. However, the step size should be chosen as noted above (for diffraction data, not model refinement). Calibration is essential to establish the neutron wavelength. The Si SRM 640b standard and several rotate under the same conditions and are used for the instrumental broadening calibration. However, the LaB6 standard should not be used, because boron is a strong linear absorber. For these reasons, it is recommended that for neutron detectors, a calibration to establish the angular offset and counting efficiency of each detector in the array is also needed. Each diffraction pattern obtained from the single detectors in an array can also be treated individually in a multiparameter Rietveld refinement. Time-of-flight neutron powder diffractometers using the time-of-flight (TOF) principle operate in a very different mode than do conventional constant-wavelength X-ray or neutron diffractometers. The
detectors are located at fixed scattering angles and the diffraction pattern is recorded as a function of the time delay from the start of a neutron burst at the source. The neutron wavelength is generally fixed by the operation of the neutron facility itself. This, in combination with the neutron flight path, will dictate the rate at which the points in the IV pattern (called the beam) are obtained during a refinement.

TOF neutron. For a neutron TOF experiment, the appearance of the diffraction pattern (including background) will depend on how the TOF data are presented. The ‘raw’ counts will generally be strongest at the short TOF end of the pattern (lowest d spacing), because the incident spectrum is strongest at short TOF. The pattern will tail off rapidly at large TOF (large d spacing), because of the fall-off in incident intensity. This gives the appearance of a high background and high Bragg intensity at short TOF. Consequently, one useful way of presenting neutron TOF data for publication is to give the intensity modified by subtracting the fitted background from both the observed intensity and the best Rietveld refinement fit and plotting the result. On the other hand, if the intensity is normalized using the incident intensity spectrum, then the background will be revealed as being nearly flat, and the Bragg peaks at longest TOF (largest d spacing) will usually be the largest ones in the pattern with the peak intensities tailing off at small TOF (low d spacing). This effect arises from the form of the Lorentz correction for TOF data, where

\[ I = \frac{d}{\sin \theta} \]  

which strongly enhances the scattered intensity for large-d spacing reflections.  

4. Peak-shape function 

Of course, an accurate description of the shapes of the peaks in a powder pattern is critical to the success of a Rietveld analysis. In a single crystal study, the refinement will not be satisfactory. The peak shapes observed are a function of both the sample (e.g. domain size, strain, etc.), the instrument (e.g. detector geometry, slit sizes), and the sample itself. Lorentzian shape is frequently used in single peak description as nontrivial and compromises are often made.

Lorentzian fits are the most common peak-shape functions investigated. The pseudo-Voigt approximation of the Voigt function is probably the most widely used for X-ray and constant-temperature neutron data (Thompson et al., 1987). The pseudo-Voigt function is simply a linear combination of Lorentzian and Gaussian components in the ratio \((\pi - 1) / 4\), where \(\pi\) is the pseudo-Voigt mixing parameter. This appears to describe the symmetrical part of an X-ray diffraction peak quite well. However, an additional function to allow a more precise description of asymmetry due to axial divergence of the diffracted beam at low angles is essential (Finger et al., 1994, and references therein). For X-ray diffraction lines, Lorentzian instrumental broadening is generally treated as a linear function, from a dominant Gaussian component at low angles to a Lorentzian trend at high angles. If a Lorentzian peak-shape function is used, the exponent \(n\) varies differently, but the same trends in line shape are observed (Louter & Langford, 1988). An advantage of using a Lorentzian model is that the Lorentzian and Gaussian components of the peak shape will be introduced in a physically intuitive way to model the overall line broadening, which furnishes valuable information about the microstructure with respect to size and strain effects. The Pearson VII function does not have this physical basis. However, both can be used to describe the peak shape for Rietveld refinement.

A pragmatic alternative to an analytical peak-shape function is an experimental or ‘learned’ one (Hepp & Baarschlocher, 1986). In this case, a single peak (one reflection) is selected from the diffraction pattern as a standard peak. This peak is fitted according to some criteria (e.g. two inflection points, one peak maximum), the calculated curve is divided into a symmetric and an asymmetric part, and these values are stored in a tabular problem. The curve can then be fitted by adding contributions from both the sample and the instrument, which has been taken from the experimental data. This, means, of course, that the individual contributions from the sample and the instrument cannot be separated as they can with a pseudo-Voigt function. The standard peak is then used to describe all of the peaks in the pattern by varying the FWHM and/or the ratio of the symmetric to the asymmetric part as a function of 2\(\theta\) (and possibly of \(h\) and/or \(k\)).

Regrettably, the type of peak-shape function selected, the range of the peak (i.e. when it no longer background becomes significant), and the ratio of the symmetric to the asymmetric part (i.e. the pattern) must be established. A rule of thumb, a peak can be considered to be background level when the intensity is less than 5% of the peak maximum. The appropriate percentage depends upon the peak shape. If the ‘tails’ of the peaks are long (i.e. high intensity shoulders), then the peak maximum is referred to as being more Gaussian than for peaks with more Gaussian character. To illustrate the difference, the percentages of the total area of experi-mental Laue view and of a purely Gaussian peak are given for different ranges in Table 1. The range needed depends upon the FWHM of the peak: thus it is usually in terms of the integral number of FWHM values, though some programs use a fraction of the peak height. Typically, the value will range from 0.20 to 0.255. FWHM depending upon the Lorentzian character of the peak. Thus, a reflection with an FWHM of 0.10 (29) contributes to the diffracted intensity over a range of at least 1.0–2.0 (29) (and sometimes much more). This param-
eter is often set at much too low a value, resulting in a severe underestimation of the reflection intensity. If the 'tails' of high-intensity reflections are cut off prematurely in the profile plot (see Fig. 1), this is a good indication that the range has been set at too small a value.

Synchronous. In general, the symmetric part of the peak-shape function is very well accounted for by the pseudo-Voigt function described above (the full Voigt convolution could give an even better fit). For very high-resolution data such as those obtained with a crystal analyzer, the instrumental contribution to the peak shape is minimal and the peaks tend to be highly Lorentzian (i.e. dominated by sample effects). For these data, an initial peak range of at least 40 FWHM is recommended. Because the intrinsic peak widths are extremely narrow, asymmetric broadening at low angles may become very pronounced and must be corrected for properly.

TOF neutron. The peak-shape functions employed for Rietveld refinement with neutron TOF data are more complex than those used for constant-wavelength neutron or X-ray data, because the neutron-pulse structure imposes an additional and asymmetric broadening effect. A simple empirical description, in which a back-to-back paired set of exponents is convoluted with the Gaussian, has been developed by Von Dreele et al. (1982).

\[ H(\Delta T) = N \times [\exp(a \times \text{erfc}(\Delta T)) + \exp(b \times \text{erfc}(\Delta T))] \]  
(2)

where \( H \) is the peak-shape function for a single reflection, \( \text{erfc} \) is the complementary error function, and the parameters \( a \) and \( b \) have various functional dependencies on the \( \Delta T \) spacing of the reflection, the scattering angle of the detector and various characteristics of the neutron source, as well as the offset of the profile point from the reflection position, \( \Delta T \).

5. Profile parameters

If only a partial structural model is available, the calculated intensities may deviate significantly from the observed ones, and this can complicate the initial refinement of profile parameters (changes in FWHM and peak asymmetry as a function of 2\( \theta \), 20 correction, unit-cell parameters). In this case, it is probably best to use a structure-free approach, in which the intensities of the reflections are simply adjusted to fit the observed ones (Le Bail, 1988), in order to obtain initial values for the profile parameters. This option (usually referred to as a Le Bail refinement), which can also be used to extract a list of integrated intensities from a powder pattern for structure determination, has now been included in most modern Rietveld programs. Sivia & David (1994) have developed an alternative to the Le Bail algorithm using least-squares refinement (Pawley, 1981) coupled with Bayesian arguments. This method enables the a.s.d.'s of the reflection intensities to be estimated more correctly and calculates the covariances between overlapping reflection parameters.

Structure refinement using this additional information is particularly useful. Whichever algorithm is used, initial values for the profile parameters can be determined. These parameters can then be further refined at a later stage when a reliable structural model has been established. If the structural model is complete and the relative intensities match the observed ones well enough, the initial profile-parameter refinement can also be performed using the structural model. In this case, the calculated pattern must first be scaled to the observed one.

Before the refinement of structural or profile parameters can be started, the positions of the observed and calculated peaks must match well. That is, the unit-cell parameters and the 20 correction (which includes both the zero offset and the deviations in 20 caused by displacement of the sample from the centre of the 20 circle) need to be refined first. These parameters can be highly correlated, and it is sometimes impossible to determine one or the other independently. This is probably best done by mixing a standard material (e.g. NIST Si standard SRM 640b) with the sample and collecting a second data-set. In this way, the 20 correction for the second measurement can be established from the Si peaks and the cell parameters of the material of interest refined. These refined cell parameters can then be used with confidence in the structure refinement using the data collected on the pure sample and any misfit in 20 can be adjusted by refining the 20 correction parameters. If an internal standard cannot be used for some reason (e.g. insufficient sample, sensitive sample, etc.), at least the 20 calibration of the instrument should be checked carefully using an external standard. If the initial cell-parameter refinement should prove to be difficult, a Le Bail (structure-free) refinement using only the low-angle data may help. For complex structures involving a high degree of reflection overlap, artificially sharpening the calculated pattern (e.g. setting FWHM values to circa 80% of their true values) will sometimes help the refinement by forcing a good fit of the maxima. However, this will only work if the peak positions are already approximately correct. It should be emphasized that unless the peak positions of the observed and calculated patterns match fairly well, Rietveld refinement cannot and will not work.

The appropriate function for the correction of 20 due to sample displacement depends upon the geometry of the instrument. For example, for Bragg-Brentano geometry with a flat-plate sample it is

\[ \Delta 2\theta = \left(2 \times \text{caht} \theta) / R \]  
(3)

where \( x \) is the displacement of the specimen and \( R \) is the radius of the goniometer circle, and for Debye-Scherrer geometry with a capillary sample it is

\[ \Delta 2\theta = (x \sin 2\theta - y \cos 2\theta) / R \]  
(4)

where \( x \) and \( y \) are the respective displacements of the capillary at 20. For 40 FWHM in 20, each once a match of the peak positions has been achieved, the other profile parameters (first peak width and then peak asymmetry as a function of 20) can be refined. The variation of the FWHM of the Gaussian component of the peak shape as a function of 20 is usually modelled with the equation derived by Caglioti et al. (1958) for low-resolution neutron data,

\[ \text{FWHM} = U \times \text{tan} \theta \times V \times \text{tan} \theta + W, \]  
(5)

and that of the Lorentzian part by

\[ \text{FWHM} = X \times \text{tan} \theta + Y / \cos \theta. \]  
(6)

While these functions are simple and usually work well, they cannot be used to model anisotropic line broadening (i.e. k-dependent line broadening) and may not describe the 20 dependence very well. In such cases, a more flexible approach (e.g. input and/or refinement of effective diffusing domain shape and anisotropic strain) is necessary. For further discussion of this topic, the reader is referred to Delhez et al. (1993), Rodriguez-Carvajal (1996), Langford & Lover (1996), Le Bail (1998), Scardi (1998) and Stephens (1999).

Incorrect profile parameters yield characteristic difference profiles, thus the examination of a suitably enlarged profile plot can be very useful in determining which parameters need further refinement. In Figs. 2–4, various misfits of a calculated profile to the observed data are illustrated for the same (somewhat asymmetric) peak. A good fit is shown in Fig. 2(a) and the effect of a pure intensity difference in Figs. 2(b) and 2(c); the effect of incorrect peak widths is shown in Fig. 3; the effect of too little peak asymmetry in Fig. 4; and the effect of a 20 mismatch in Fig. 5. In a real refinement, the misfits are rarely caused by a single variable and so the samples of combinations of incorrect profile parameters are given in Fig. 6.


definition of the lattice parameters and zero offset generally presents no problems, especially when sample-displacement errors are eliminated by the use of CA or Soller slit geometry. When area detectors are used, very specialized techniques of data processing are required to produce a standard powder profile and there may be additional sources of error that are beyond the scope of this discussion. Because of the predominantly Lorentzian character of high-resolution data, refinement of the Lorentzian half-width parameters \( Y \) and \( R \) is usually straightforward, but unconstrained refinement of the Gaussian parameters \( U \), \( V \) and \( W \) may lead to nonphysical results, or at worst, complete failure of the refinement. In such cases, some kind of constraint function should be applied, or the
parameters fixed at the instrumental values. Because of the very narrow peak widths, anisotropic line broadening is much more likely to be visible in a synchrotron experiment and careful attention must be given to the choice of a suitable model.

**Constant-wavelength neutron.** The peak-shape function used for constant-wavelength neutron diffraction data are essentially the same as those described for X-rays. However, $U$, $V$ and $W$ make a far more dramatic contribution to the profile because constant-wavelength neutron diffractometers have much lower resolution than do constant-wavelength X-ray instruments. A plot of FWHM versus $(d, \theta \tan \theta$, etc.) is more parabolic and the line shapes are more Gaussian because of the dominant instrumental contribution. In contrast to the X-ray case, $U$, $V$ and $W$ are easily determined by Rietveld refinement.

6. Completing the structural model

If the structural model is incomplete, difference Fourier maps can be used to locate the missing atoms. In general, refinement of structural parameters should not be started at all (or almost all) atoms have been found. Otherwise, refinement is likely to lead to a false minimum, because the algorithm will attempt to describe all of the electron density with too few atomic positions.

With a partial structural model, the distribution of the intensities of reflections overlapping in the powder pattern can be estimated by assuming that the distribution is the same as that calculated for the partial model. Such a partitioning of the overlapping reflections is easily done in a Rietveld program, because the same procedure is used to calculate the $R$ values (see below). The more complete the model, the more valid this approximation. In this way, a pseudo-single-crystal data set (a list of the $hkl$'s and their corresponding intensities) can be produced and an approximate electron-density map (albeit model biased) generated using a Fourier transform (using phases calculated from the partial model). In general, maps calculated from powder data are more diffuse than those calculated from single-crystal data, but they are still quite usable. It should be borne in mind that they are doubly biased towards the structural model, because both the phases (as in the single-crystal case) and the intensity partitioning are taken from the model. By subtracting the electron density calculated for the model from that calculated using the observed reflection intensities, a difference Fourier map (difference electron-density map), which highlights the electron density not accounted for in the model, is produced. Truncation errors are less pronounced in a difference map than in an electron-density map (generated using just the $F_{hkl}$), because the missing $\Delta F$'s are approximately zero, whereas the missing $F_{hkl}$'s are not. It is worth mentioning that maps obtained from a maximum entropy reconstruction (see, for example, Kumazawa et al., 1993) are usually less noisy than Fourier maps and may show the missing features more clearly.

7. Refining the structure

With a complete structural model and good starting values for the background contribution, the unit-cell parameters and the profile parameters, the Rietveld refinement of structural parameters can begin. Because the global minimum of the least-squares residual function is much shallower with powder data than it is with single-crystal data, and false minima are more prevalent, the refinement needs constant monitoring. A refinement of a structure of medium complexity can require a hundred cycles, while a structure of high complexity may easily require several hundred. Refinement is usually done in sets of two to five cycles at a time. To monitor the progress of a refinement, the two most useful pieces of information are the profile fit and the nature of the parameters shifts (i.e. shift/evol.; are the shifts oscillating, diverging or converging?). The profile fit is best seen in a plot of the observed and calculated patterns, but can also be followed numerically with a reliability factor or $R$ value (see below). It should be emphasized that profile plots are much more informative than $R$ values for guiding a refinement. The difference plots indicate whether a high $R$ value is due to a profile-parameter problem (i.e. total intensity is approximately correct but there are differences in the peak form; see Figs. 1-6), or to a deficiency in the structural model (i.e. integrated intensities do not match).

It is difficult to cover all the details of a full refinement, but an approximate strategy can be described. Changes in positional parameters cause changes in structure-factor magnitudes and therefore in relative peak intensities, whereas atomic displacement (thermal) parameters have the effect of emphasizing the high-angle region (smaller thermal parameters) or de-emphasizing it (larger thermal parameters). It is usually

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**TOP neutron.** The more complex Bragg peak shape for TOP neutron data (Von Dreele et al., 1982) can be described using a number of instrument-dependent coefficients, which can be established by Rietveld refinement with data from standard materials. The minimum-sample position bias in the lattice parameters obtained from Rietveld refinement of neutron TOP data is found in the pattern from the set of detectors at the highest angle. Consequently, the effect can be minimized in a multi-data-set refinement by allowing all 'differential operator constants', except that of the highest-angle detectors, to vary simultaneously with the lattice parameters.

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advisable to start the refinement of structural parameters with the positions of the heavier atoms and then to try those of the lighter atoms. If the latter refinement corrects the model to the extent that the model can then be refined simultaneously. At this point, the refinement of the somewhat trickier parameters can be attempted. The refined parameters are refined consecutively, the parameters anisotropically. Refinement of the thermal parameters are correlated and may be refined simultaneously. Practice shows that it is sufficient to refine the parameters of the thermal parameters (heavier atoms first) can be attempted, but this can be difficult with X-ray powder data, especially if the 20 range is small. Because there is no sin(θ) dependence of the scattering cross sections with neutrons, thermal-parameter refinement with neutron data is usually more reliable and any anisotropic refinement is sometimes possible. With X-rays, it is perhaps prudent to constrain the thermal parameters for similar atoms to be equal (at least in the early stages) and thereby reduce the number of thermal parameters required. Occurrence parameters are correspondingly difficult to refine and chemical constraints (e.g. relative occupations of atoms in a known fragment) should be applied whenever possible. If these parameters are appropriate for the correct interpretation of the structure, simultaneous refinement of multiple data-sets (e.g. one X-ray and one neutron pattern or two X-ray patterns collected at different wavelengths, which change the 'anomalous' scattering properties of one or more atoms) should be considered. By refining a single structure using two independent data-sets containing complementary information, problems of parameter correlation can sometimes be minimized. However, care must be taken that the conditions for both data collections are as similar as possible (e.g. temperature, atmosphere, same sample, etc.), or the joint refinement will not work. Refinement of the profile parameters with the structural parameters is also recommended.

The structure should converge to a minimum. That is, the maximum shift/s.d. in the final cycle of refinement should be no more than 0.10 (see below for a discussion of profile parameters (profile and structural) should be refined simultaneously to obtain correct estimated standard deviations.

8. Restraints

Because powder diffraction data are a one-dimensional projection of three-dimensional data, they suffer from an inherent loss of information. One way to compensate for this loss, at least in part, is to supplement the diffraction data with information from another source. Geometric information (typical bond distances and angles) gleaned from related structures lends itself to such an approach. The information can be used in a Rietveld refinement in two different ways: to increase the number of observations (second data-set consisting of geometric 'observations') or to reduce the number of parameters (e.g. a rigid body). The former is generally preferred because it is easier to implement. The use of geometric restraint matrices in this way not only increases the number of observations, thereby allowing more parameters to be refined, it also keeps the geometry of the structural model sensible.

The set of geometric 'observations' is simply treated as a second data-set and the quantity minimized in the refinement is:

\[ S = S_0 + c_S S_1 \]  

where \[ S_0 \] is the weighted difference between the observed \( y(\text{obs}) \) and calculated \( y(\text{calc}) \) diffraction patterns (Rietveld residual),

\[ S_1 = \sum w_1 y(\text{obs}) - y(\text{calc})^2 \]  

and \( c_S \) is a factor that allows a weighting of the geometric observations 'data-set' with respect to the diffraction data-set. In general, the weighting factor \( c_S \) is set high at the beginning of a refinement when the structure is incomplete or only approximately correct, because the interatomic distances easily become unreasonably long or short at this stage. It can then be reduced during the course of the refinement as the structural model improves.

Experience has shown that if the geometric assumptions are invalid (e.g. a tetrahedral coordination has been assumed, but an octahedral one is actually present), the refinement will not progress satisfactorily. In this case, the restraints need to be examined and reconsidered. Geometric restraints, if used carefully, can enhance a refinement considerably, allowing otherwise impossible complex structures to be refined successfully. It is imperative, however, that the final structural model fit both the geometric and the X-ray data satisfactorily.

9. Number of observations (and number of parameters)

It is difficult to quantify the amount of structural information in a powder diffraction pattern. The intensity at each step along the profile has been measured and, mathematically, each measurement is an observation in the core least-squares algorithm of a Rietveld refinement program. However, only the integrated intensities of the individual reflections can be considered unique observations for the refinement of structural parameters, and these are determined with varying degrees of precision and accuracy depending upon the counting time, the number of steps across the peak (each step represents an independent measurement of the integrated intensity of that reflection) and the amount of refinement overlap involved. While it is easy to see that two reflections with the same 20 value result in a single peak, and therefore can only be considered to be a single observation, it is less clear how many observations there are when there are two reflections with similar but not identical 20 values. Yet it is important to have some estimate of the amount of information in the pattern in order to judge how many structural parameters can be refined sensibly. The Rietveld algorithm will allow many more parameters to be refined than the data can actually support (because mathematically the number of observations is the number of steps in the profile), so the user has to intervene with common sense. If too many structural parameters have been refined, the fit should be reflected in very large standard deviations (see below).

Altomare et al. (1995) have devised a method for estimating the effective number of observations based on the percentage of the area of a reflection that does not overlap with another reflection. While this approach may not have a rigorous basis, it does give the user a reasonable estimate of the number of refinable parameters that the data will support. The observation parameter ratio should be at least three and preferably five.

10. Estimated standard deviations

It is important to know that the various Rietveld refinement programs calculate e.s.d.'s differently. That is, given the same data and the same structural model, one program will not necessarily produce the same e.s.d.'s for the structural parameters as another. This situation is a result of different interpretations of how the errors are best estimated. From a purely statistical point of view, each measurement is an independent observation and inter-station correlations at different points on the same peak are simply two independent measurements of the intensity of that peak. This is then directly comparable to a single-crystal data-set in which symmetry-equivalent reflections are present or in which the same reflection has been measured more than once. It is important to emphasize that the e.s.d.'s calculated assume that counting statistics are the only source of error. Systematic errors (e.g. bias introduced by some undescribed physics in the experiment or an inadequate background, peak-shape or structural model), which are in fact significant, cannot be estimated. The e.s.d.'s reflect the precision of the refined parameters and not their accuracy. Several of the methods used to calculate the e.s.d.'s deviate from this strict statistical logic in an attempt to allow for systematic errors in the structural model.

A powder diffractionist needs to know which method is used to calculate the e.s.d.'s in the Rietveld program to be used and to be aware that opinions vary regarding the most appropriate method; for most purposes that is sufficient. In any publication, the method used to calculate the e.s.d.'s should be stated. It is also important to know how the e.s.d.'s of derived parameters (e.g. interatomic distances and angles calculated from the atomic coordinates) are calculated. The whole correlation matrix, not just the diagonal elements, should be included in the calculation. In cases where the e.s.d.'s are critical to the correct interpretation of small differences (e.g. oxidation states, occupancy parameters or unusual bond lengths that might indicate unusual chemistry), the reader is referred to the papers by Prince (1981, 1983), Scott (1983), Hill & Fluck (1987), Antoniadis et al. (1990), Bébar (1992) and Cox & Poprawski (1996).

11. R values

Although a difference profile plot is probably the best way of following and guiding a Rietveld refinement, the fit of the calculated pattern to the observed data can also be given numerically. This is usually done in terms of agreement indices or R values. The weighted-profile R value, \( R_w \), is defined as

\[ R_w = \sqrt{\frac{\sum w_1 y(\text{obs}) - y(\text{calc})^2}{\sum w_1 y(\text{obs})^2}} \]  

where \( y(\text{obs}) \) is the observed intensity at step \( i \), \( y(\text{calc}) \) the calculated intensity, \( w_1 \) the weight. The summation in the numerator is the value that is minimized during a Rietveld refinement. If the background has been subtracted, \( y(\text{obs}) \) is the net intensity after subtraction, but if the background is refined, \( y(\text{obs}) \) and \( y(\text{calc}) \) is likely to include the background contribution. In the latter case, a high background will automatically produce a low \( R_w \) value, because a significant part of the intensity is accounted for by the background function. Thus, the comparison of profile \( R \) values from different kinds of powder diffraction experiments can be extremely misleading. For example, \( R_w \) for neutron TOF data are often quite small (e.g. a few %), while those for laboratory X-ray data are larger (e.g. ~10%). This is primarily due to the level of the background. In order to evaluate how well the peaks (which contain the structure-sensitive information) are fitted, \( R_w \) with a background contribution calculated should also be calculated. Most programs include this feature. In any publication, the type of agreement index used must be clearly specified.

Ideally, the final \( R_w \) should approach the statistically expected R value, \( R_{ew} \):

\[ R_{ew} = \sqrt{\frac{N - P}{P}} \sum w_1 y(\text{obs})^2 \]  

where \( N \) is the number of observations, \( P \) the number of parameters, and \( w_1 \) the weight.
where $N$ is the number of observations and $P$ the number of parameters. $R_{	ext{m.r.}}$ reflects the quality of the data (i.e. the counting statistics). Thus, the ratio between the two (goodness of fit),

$$\chi^2 = R_{	ext{m.r.}}/R_{	ext{m.r.}}$$

which is also quoted quite often in the literature, should approach 1. If the data have been ‘over-collected’ (i.e. errors are no longer dominated by counting statistics), $R_{	ext{m.r.}}$ will be very small and $\chi^2$ for a fully refined structure, much larger than 1. Conversely, if the data have been ‘under-collected’ (i.e. collected too quickly), $R_{	ext{m.r.}}$ will be large and $\chi^2$ could be less than 1. Strange $\chi^2$ values can also arise from data for which the s.e.d.'s of the counts have been incorrectly calculated (e.g. counts given as counts per second are assumed to be the absolute counts). The final $R_{	ext{m.r.}}$ obtained in a structure-free refinement (e.g. using the Le Bail algorithm) is a good indication of the best profile fit of the data that can be obtained, and the $R_{	ext{m.r.}}$ in the Rietveld (structural) refinement should approach it.

An $R$ value similar to that reported for single-crystal refinements, based on the agreement between the ‘observed’ and calculated structure factors, $F_{\text{calc}}$, can also be calculated by distributing the intensities of the overlapping reflections according to the structural model

$$R = \sum |F_{\text{obs}} - F_{\text{calc}}| / \sum |F_{\text{obs}}|$$

This is of course, biased towards the structural model, but it gives an indication of the reliability of the structure. This quantity is not used actively in the refinement, but should decrease as the structural model improves during the course of the refinement. Similarly, the Bragg-intensity $R$ value

$$R = \sum |I_{\text{obs}} - I_{\text{calc}}| / \sum |I_{\text{obs}}|$$

where $I_{\text{obs}} = nF^2_{\text{obs}}$ (multiplied by $n = 2n$), or its weighted equivalent (Cox & Papoular, 1996) can be used to monitor the improvement in the structural model. $R$ values are useful indicators for the evaluation of a refinement, especially in the case of small improvements to the model, but they should not be overinterpreted. The most important criteria for judging the quality of a Rietveld refinement are (i) the fit of the calculated pattern to the observed data and (ii) the chemical sense of the structural model. The former can be evaluated on the basis of the final profile plot (using the complete range of a few collected reflections), the latter on a careful examination of the final atomic parameters. Any publication reporting the results of a Rietveld refinement should include a plot of the observed intensities, the calculated profile and the difference curve. For X-ray data, the intensity scale for the high-angle range, where the observed intensities are very low, should be magnified. Interatomic distances (both bonding and nonbonding) should be reasonable, bond angles sensible and population parameters consistent with the chemical composition of the material. Further, the structural model should be consistent with the results of other characterization techniques such as infrared, Raman, ultraviolet, NMR, EPR (electron paramagnetic resonance) and/or mass spectrometry, thermogravimetric and/or chemical analysis, electron microscopy, optical or magnetic measurements, etc. Any unusual features in the structural model should be probed using such independent techniques.

### 12. Some common problems and where to look for the solution

Each structure refinement has its own idiosyncrasies and will present problems that require imaginative solutions. However, some problems are of a more general nature and arise in many cases. Probably the most frequent source of difficulty in a Rietveld refinement is an inadvertent error in the input file for the refinement program. If the input file appears to be correct (i.e. the program is in fact doing what you think you told it to do) and the data themselves have been examined critically for possible errors, then perhaps the suggestions below for tackling specific problems will be of some assistance.

12.1. The background is not well fitted

Try a different function, background subtraction, or a combination of the two.

12.2. The peak shapes are poorly described

(i) Check the difference plot to see if one of the characteristic difference profiles shown in Figs. 2-6 occurs systematically, indicating that a specific profile parameter should be refined or further refined. (ii) Try a different peak-shape function. (iii) Check that there is an asymmetry correction in the peak-shape function. (iv) Check to see if the peak widths are hkl dependent and require a more sophisticated function to describe the $2\theta$ dependence. A plot of FWHM values of resolved reflections as a function of $2\theta$. Furthermore, highly general indicate whether or not structural imperfections are causing anisotropic line broadening (e.g. anisotropic size and/or strain, stacking fault) and which functions are best described to describe the angular dependence (see Delhez et al., 1993).

12.3. There is a mismatch between the peak positions in the calculated and observed patterns

(i) Determine the unit-cell parameters with an independent measurement using an internal standard. (ii) Check that the $2\theta$ correction (zero offset and sample displacement) function used is appropriate for the diffractometer geometry.

12.4. The tails of the peaks in the calculated pattern seem to be cut off prematurely

Try increasing the peak range used in the calculation.

12.5. The relative intensities of a few reflections are too high but none too low

Check the sample used for data collection. This may indicate a problem with poor particle statistics (i.e. ‘rocks in the dust’). The only solution is to recolect the data after regrinding/sieving the sample (and spinning the sample during data collection).

12.6. There are small unindexed peaks in the diffraction pattern

(i) If other preparations of the same material have these peaks with similar relative intensities, they are probably not due to an impurity (though it should be verified that these peaks do not arise from the sample holder because the infinite-thickness condition is not fulfilled or because the sample holder moves during a variable-temperature study). Does one (or more) of the unit-cell axes need to be doubled or tripled? Check the space group: can the peaks be indexed in a subgroup of the selected space group? Are other space groups consistent with the assumed systematic absences? How well established are the systematic absences? Are others possible? (ii) If other preparations of the same material do not have these peaks or have them with different relative intensities, they probably belong to a second phase. Try indexing them as a set: try to identify the phase. If its structure is known, try a two-phase refinement.

12.7. The refinement does not converge

(i) Look at the observed and calculated profiles carefully. Is the observed peak shape well defined by the profile parameters? Do the peak positions match? Is the background correction sensible? Is the scale factor correct? (ii) Is the structural model complete? If not, try to locate the missing atoms by generating a difference Fourier map before beginning to refine structural parameters. (iii) Check for oscillations in the parameter shifts and apply damping factors as needed. (iv) Examine the covariance matrix for correlations between parameters. If high correlation is present between two variables (and not the scale factor) then a fixed scaling factor can be used. (v) Check the variation in the atomic parameters after relaxation can be checked against the performance of the refinement (such as the profile R-factors). (vi) If geometric restraints are not used, then look for correlations between geometric restraints (which increase the number of observations), try using rigid-body descriptions (which reduce the number of parameters). (vii) Set thermal (atomic displacement) parameters at sensible values and hold them fixed (or constrain similar atoms to have identical displacement parameters). (x) Try a different space group. (xi) Is the problem fundamentally wrong with the model? (xii) Do the data support the number of parameters being refined?

12.8. The final structure is not chemically sensible (impossible interatomic distances or displacement factors)

(i) Try using restraints to keep interatomic distance sensible and increase the weight of the restraints if necessary. (ii) Delete the offending atoms and try generating a difference Fourier map (or a maximum entropy reconstruction) to relocate them. (iii) Try starting from a sensible geometry and refining the structure more cautiously. (iv) Reconsider the model, the restraints and the space group. (v) Try fixing thermal (atomic displacement) parameters at sensible values (or constrain similar atoms to have identical thermal parameters).

12.9. Refinement converged, but there is an angle-dependent intensity mismatch and/or unreasonable thermal parameters

(i) Check the Lorentz-polarization correction. (ii) Should an absorption correction be applied? (iii) Is a surface-roughness correction indicated? (iv) Have the atoms been identified correctly? (v) Check the scattering factors used (especially if they have been input by hand). (vi) Is there preferred orientation in the sample?

13. Conclusions

Structure refinement using the whole-pattern or Rietveld method is a powerful technique for extracting structural details from powder diffraction data. With modern methods, structures with up to 200 structural parameters can be refined successfully, if care is taken and the data are of sufficiently high quality. This review does not cover all the consequences and pitfalls of some of the practical aspects of the technique. Small details play an important role in structure analysis using the Rietveld method and at the moment there are no detailed books, though often tedious, is usually rewarded with success.

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