Crystal Structure Determination I

Dr. Falak Sher

Pakistan Institute of Engineering and Applied Sciences

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Crystal Structure Determination

The determination of an unknown structure proceeds in three major steps:

1. **The shape and size of the unit cell are deduced from the angular positions of the diffraction lines.**
2. **The number of atoms per unit cell is then computed from the shape and size of the unit cell, the chemical composition of the specimen, and its measured density.**
3. **Finally, the position of the atoms within the unit cell are deduced from the relative intensities of the diffraction lines.**

The third step is generally the most difficult and there are many structures which are known only incompletely, in the sense that this final step has not yet been made.

Size and Shape of the Unit Cell

This step is same as the indexing of power diffraction pattern. It involves:

- **The accurate determination of peak positions.**
- **Determination of the unit cell parameters from the peak positions.**
  - **Bragg's Law**
  - **Interplanar d-spacing**
  - **Systematic Absences**

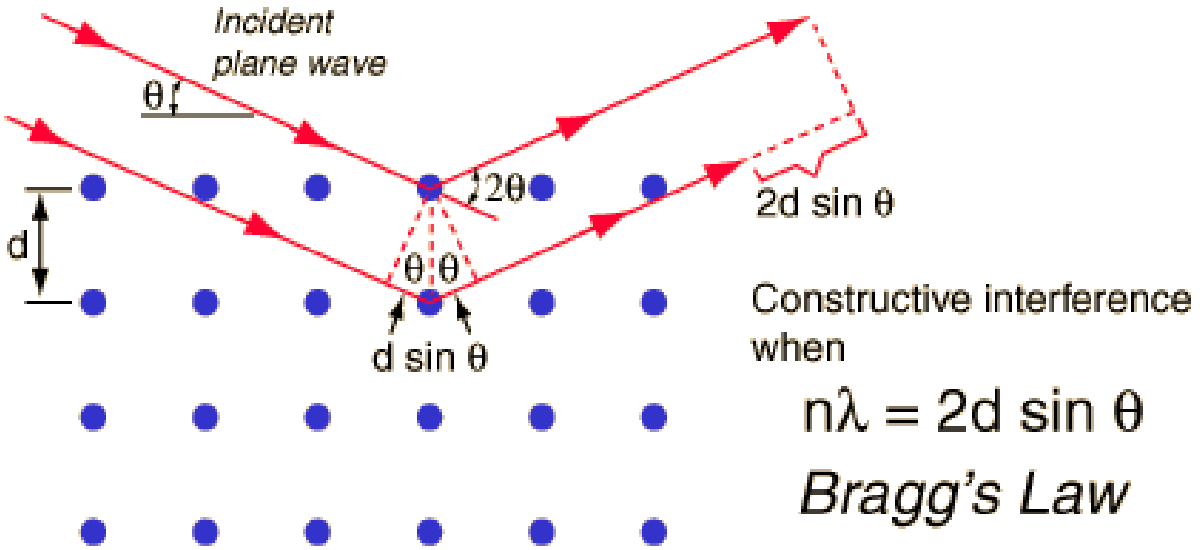
Bragg's Law

When x-rays are scattered from a crystal lattice, peaks of scattered intensity are observed which correspond to the following conditions:

1. **The angle of incidence = angle of scattering.**
2. **The pathlength difference is equal to an integer number of wavelengths.**

The condition for maximum intensity contained in Bragg's law above allow us to calculate details about the crystal structure, or if the crystal structure is known, to determine the wavelength of the x-rays incident upon the crystal.

$$n\lambda = 2d\sin\theta$$ *Bragg's Law*

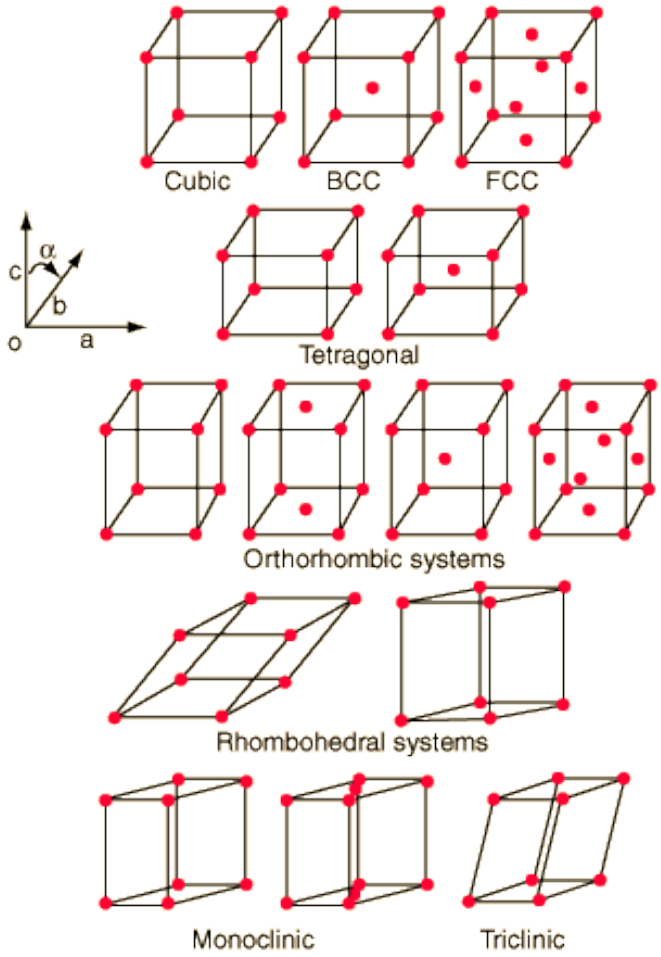


Bravais lattices

Crystals possess a regular, repetitive internal structure. The concept of symmetry describes the repetition of structural features.

Symmetries are most frequently used to classify the different crystal structures. In general one can generate 14 basic crystal structures through symmetries. These are called Bravais lattices. Any crystal structures can be reduced to one of these 14 Bravias lattices.

Name	Number of Bravais lattices	Conditions
Triclinic	1	$a_1 \neq a_2 \neq a_3$, $\alpha \neq \beta \neq \gamma$
Monoclinic	2	$a_1 \neq a_2 \neq a_3$, $\alpha = \beta = 90° \neq \gamma$
Orthorhombic	4	$a_1 \neq a_2 \neq a_3$, $\alpha = \beta = \gamma = 90°$
Tetragonal	2	$a_1 = a_2 \neq a_3$, $\alpha = \beta = \gamma = 90°$
Cubic	3	$a_1 = a_2 = a_3$, $\alpha = \beta = \gamma = 90°$
Trigonal	1	$a_1 = a_2 = a_3$, $\alpha = \beta = \gamma < 120° \neq 90°$
Hexagonal	1	$a_1 = a_2 \neq a_3$, $\alpha = \beta = 90°$, $\gamma = 120°$



d-spacing

Cubic:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

Tetragonal:

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

Hexagonal:

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$$

Rhombohedral:

$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2)\sin^2\alpha + 2(hk + kl + hl)\cos^2\alpha - \cos\alpha)}{a^2(1 - 3\cos^2\alpha + 2\cos^3\alpha)}$$

Orthorhombic:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

d-spacing, cont.

Monoclinic:
$$\frac{1}{d^2} = \frac{1}{\sin^2\beta}\left(\frac{h^2}{a^2} + \frac{k^2\sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right)$$

Triclinic:
$$\frac{1}{d^2} = \frac{1}{V^2}(S_{11}h^2 + S_{22}k^2 + S_{33}l^2 + 2S_{12}hk + 2S_{23}kl + 2S_{13}hl)$$

In the equation for triclinic crystals,

V = volume of unit cell (see below),

$$S_{11} = b^2c^2\sin^2\alpha,$$

$$S_{22} = a^2c^2\sin^2\beta,$$

$$S_{33} = a^2b^2\sin^2\gamma,$$

$$S_{12} = abc^2(\cos\alpha\cos\beta - \cos\gamma),$$

$$S_{23} = a^2bc(\cos\beta\cos\gamma - \cos\alpha),$$

$$S_{13} = ab^2c(\cos\gamma\cos\alpha - \cos\beta).$$

Q. The crystal structure of $SrTiO_3$ is cubic, space group Pm3m with a unit cell edge a = 3.90 Å. Calculate the expected 2θ positions of the first three peaks in the diffraction pattern, if the radiation is Cu K_α (λ = 1.54 Å).

A.

1. Recognize the *hkl* values for the first few peaks:
   100, 110, 111, 200, 210, 211, 220, etc.
2. Calculate the interplanar spacing, d, for each peak:
   $1/d^2 = (h^2 + k^2 + l^2)/a^2$
3. Use Bragg's Law to determine the 2θ value:
   $\lambda = 2d_{hkl} \sin \theta_{hkl}$

   ***hkl* = 100**

   $1/d^2 = (1^2 + 0^2 + 0^2)/(3.90\ Å)^2 \rightarrow d = 3.90\ Å$

   $\sin \theta_{100} = 1.54\ Å/\{2(3.90\ Å)\} \rightarrow \theta = 11.4°\ (2\theta = 22.8°)$

   ***hkl* = 110**

   $1/d^2 = (1^2 + 1^2 + 0^2)/(3.90\ Å)^2 \rightarrow d = 2.76\ Å$

   $\sin\theta_{110} = 1.54\ Å/\{2(2.76\ Å)\} \rightarrow \theta = 16.2°\ (2\theta = 32.4°)$

   ***hkl* = 111**

   $1/d^2 = (1^2 + 1^2 + 1^2)/(3.90\ Å)^2 \rightarrow d = 2.25\ Å$

   $\sin \theta_{111} = 1.54\ Å/\{2(2.25\ Å)\} \rightarrow \theta = 20.0°\ (2\theta = 40.0°)$

INDEXING DIFFRACTION PATTERNS

Powder Diffraction: Indexing

- **Indexing is the process of determining the unit cell parameters from the peak positions. To index a powder diffraction pattern it is necessary to assign Miller indices, *hkl*, to each peak.**
- **A diffraction pattern cannot be analyzed until it has been indexed. It is always the first step in analysis.**
- **Unfortunately it is not just the simple reverse of calculating peak positions from the unit cell dimensions and wavelength.**
- **We will show how one can manually index diffraction patterns of high symmetry structures. For lower symmetry structures (monoclinic, triclinic) it is usually necessary to use a computer algorithm. This is called *Autoindexing*.**
- **The information in an XRD pattern is a direct result of two things:**

1. **The *size* and *shape* of the unit cells, which determine the *relative positions* of the diffraction peaks.**
2. ***Atomic positions* within the unit cell, which determine the *relative intensities* of the diffraction peaks**

PART1:
INDEXING A DIFFRACTION PATTERN FROM CUBIC MATERIALS

Bragg's Law tells us the location of a peak with indices *hkl*. θ_{hkl} is related to the interplanar spacing, *d*, as follows:

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

$$1/d = 2 \sin \theta / \lambda$$

$$1/d^2 = 4 \sin^2 \theta / \lambda^2$$

We know that for a cubic phase the *d*-values can be calculated from the *Miller indices* (*hkl*):

$$1/d^2 = (h^2 + k^2 + l^2)/a^2$$

Combining these two equations we get the following relationship

$$(h^2 + k^2 + l^2) / a^2 = 4\sin^2\theta / \lambda^2$$

or

$$\sin^2\theta = (\lambda^2 /4a^2)(h^2 + k^2 + l^2)$$

Where λ and *a* are constants, hence $\lambda^2 /4a^2$ is constant.

$\mathrm{Sin}^2\theta$ is proportional to $h^2 + k^2 + l^2$ i.e., planes with higher *Miller indices* will diffract at higher values of θ.

In cubic systems, the first XRD peak in the diffraction pattern will be due to diffraction from planes with the lowest *Miller indices*

– simple cubic, (100), $h^2 + k^2 + l^2 = 1$

– body-centered cubic, (110), $h^2 + k^2 + l^2 = 2$

– face-centered, (111), $h^2 + k^2 + l^2 = 3$

- **If the lattice is not primitive certain classes of *hkl* peaks will be missing. These are called *systematic absences* and we can use them to determine the space group (or at least narrow down the possibilities).**

Conditions for allowed reflection for cubic lattices:

Primitive:

All possible *h*, *k* and *l* values

Body-centered:

reflection is allowed when ($h + k + l$) is even

reflection is not allowed when ($h + k + l$) is odd

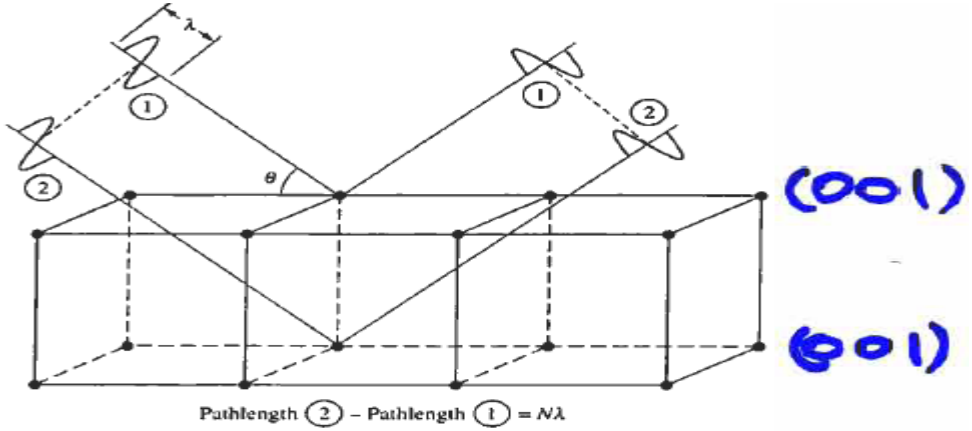
Face-centered:

reflection is allowed when *h*, *k* and *l* are either all even or all odd

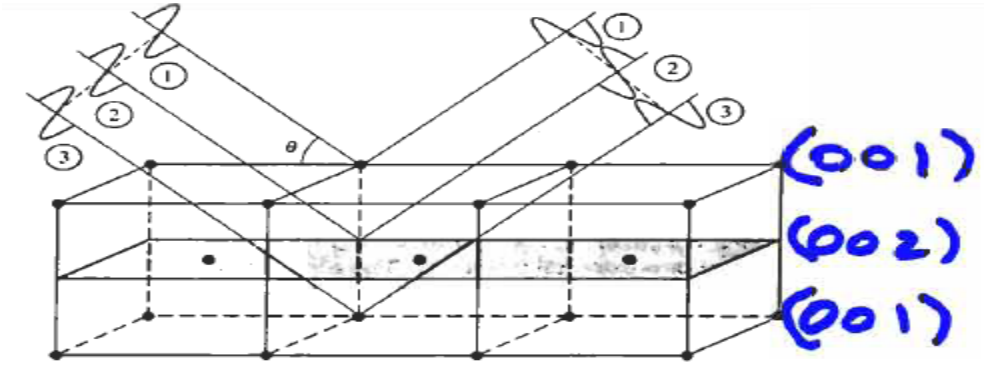
no reflection when *h*, *k* and *l* are mixed i.e., even and odd

Hence,

- **Primitive $h^2 + k^2 + l^2$ = 1,2,3,4,5,6,8,9,10,11,12,13,14,16…**
- **Body-centered $h^2 + k^2 + l^2$ = 2,4,6,8,10,12,14,16…**
- **Face-centered $h^2 + k^2 + l^2$ = 3,4,8,11,12,16,19,20,24,27,32…**



Pathlength (2) – Pathlength (1) = $N\lambda$



Pathlength (3) – Pathlength (1) = $n\lambda$

Pathlength (3) – Pathlength (2) = Pathlength (2) – Pathlength (1) = $\left(\frac{2n-1}{2}\right)\lambda$

Systematic Absences– Screws & Glides

Screw axes and glide planes also have elements of translation and they will give systematic absences as well. Some examples are given below.

Centering Allowed peaks

2_1 screw axis || to a → h00 peaks are only allowed when h is an even #
2_1 screw axis || to b → 0k0 peaks are only allowed when k is an even #
2_1 screw axis || to c → 00l peaks are only allowed when l is an even #
3_1 screw axis || to c → 00l peaks are only allowed when l = 3n (n = integer)
4_1 screw axis || to c → 00l peaks are only allowed when l = 4n (n = integer)

a glide plane ⊥ c → hk0 peaks are only allowed when h is an even #
b glide plane ⊥ c → hk0 peaks are only allowed when k is an even #
n glide plane ⊥ c → hk0 peaks are only allowed when h+k is an even #
a glide plane ⊥ b → h0l peaks are only allowed when h is an even #
c glide plane ⊥ b → h0l peaks are only allowed when l is an even #
n glide plane ⊥ b → h0l peaks are only allowed when h+l is an even #

Selection Rules for Reflections in Cubic Crystals

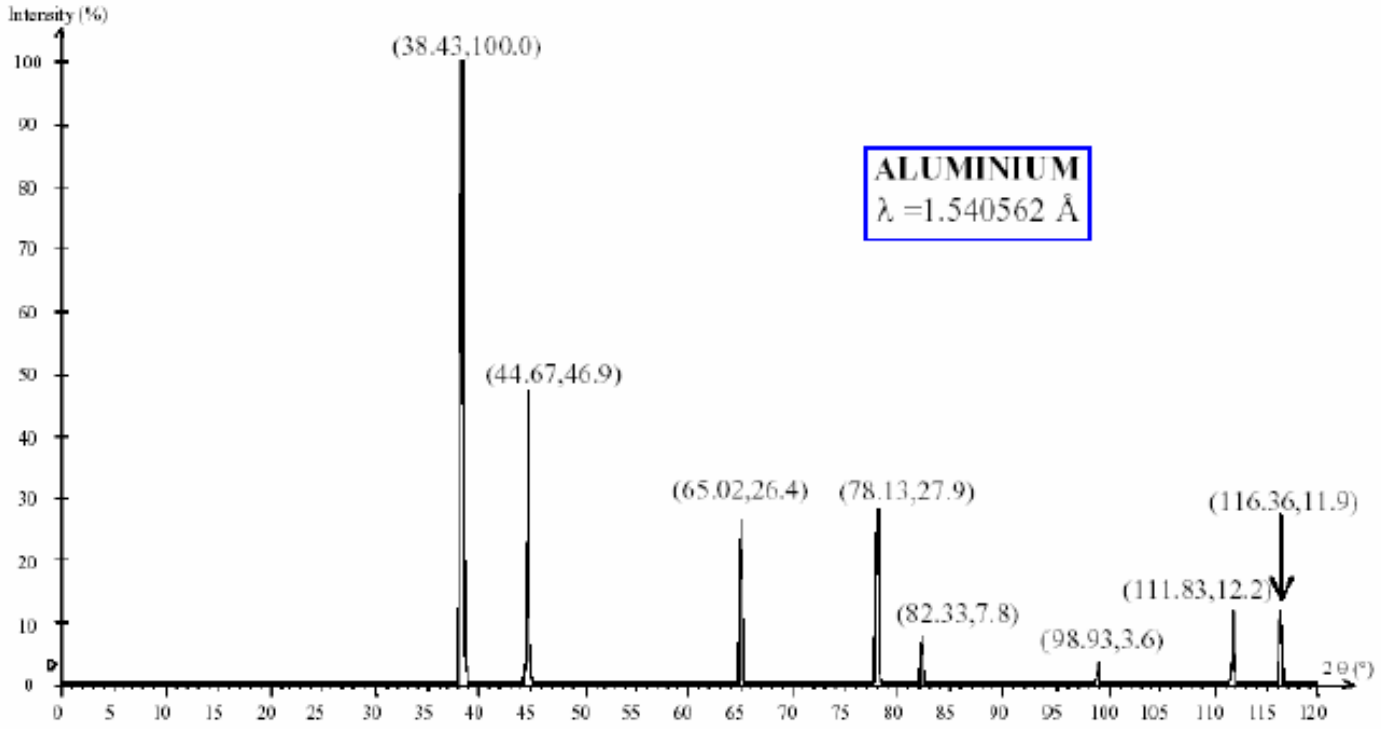
(*hkl*)	$h^2 + k^2 + l^2$	SC	BCC	FCC
100	1	√	×	×
110	2	√	√	×
111	3	√	×	√
200	4	√	√	√
210	5	√	×	×
211	6	√	√	×
220	8	√	√	√
300, 221	9	√	×	×
310	10	√	√	×
311	11	√	×	√
222	12	√	√	√
320	13	√	×	×
321	14	√	√	×
400	16	√	√	√
410, 322	17	√	×	×
411, 330	18	√	√	×
331	19	√	×	√
420	20	√	√	√
421	21	√	×	×

Two Methods of Indexing

1. **Mathematical**
2. **Analytical**

Worked Example

Consider the following XRD pattern for Aluminum, which was collected using CuKα radiation.



Index this pattern and determine the lattice parameters.

Worked Example cont…

Steps:

(1) Identify the peaks.

(2) Determine $\sin^2\theta$

(3) Calculate the ratio $\sin^2\theta / \sin^2\theta_{min}$ and multiply by the appropriate integers.

(4) Select the result from (3) that yields $h^2 + k^2 + l^2$ as an integer.

(5) Compare results with the sequences of $h^2 + k^2 + l^2$ values to identify the Bravais lattice, e.g. BCC $h^2 + k^2 + l^2 = 2,4,6,8,\ldots$

(6) Calculate lattice parameters.

Worked Example cont…

Step 1: Identify the peaks and their proper 2θ values. Eight peaks for this pattern.

Peak No.	2θ	$\sin^2\theta$	$1\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$2\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$3\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$h^2+k^2+l^2$	hkl	a (Å)
1	38.43							
2	44.67							
3	65.02							
4	78.13							
5	82.33							
6	98.93							
7	111.83							
8	116.36							

Worked Example cont…

Step 2: Determine $\sin^2\theta$

Peak No.	2θ	$\sin^2\theta$	$1\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$2\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$3\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$h^2+k^2+l^2$	hkl	a (Å)
1	38.43	0.1083						
2	44.67	0.1444						
3	65.02	0.2888						
4	78.13	0.3972						
5	82.33	0.4333						
6	98.93	0.5776						
7	111.83	0.6859						
8	116.36	0.7220						

Worked Example cont…

Step 3: Calculate the ratio $\sin^2\theta / \sin^2\theta_{min}$ and multiply by the appropriate integers.

Peak No.	2θ	$\sin^2\theta$	$1\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$2\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$3\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$h^2+k^2+l^2$	hkl	a (Å)
1	38.43	0.1083	1.000	2.000	3.000			
2	44.67	0.1444	1.333	2.667	4.000			
3	65.02	0.2888	2.667	5.333	8.000			
4	78.13	0.3972	3.667	7.333	11.000			
5	82.33	0.4333	4.000	8.000	12.000			
6	98.93	0.5776	5.333	10.665	15.998			
7	111.83	0.6859	6.333	12.665	18.998			
8	116.36	0.7220	6.666	13.331	19.997			

Worked Example cont…

Step 4: Select the result from (3) that yields $h^2 + k^2 + l^2$ as a series of integers.

Peak No.	2θ	$\sin^2\theta$	$1\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$2\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$3\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$h^2+k^2+l^2$	hkl	a (Å)
1	38.43	0.1083	1.000	2.000	3.000			
2	44.67	0.1444	1.333	2.667	4.000			
3	65.02	0.2888	2.667	5.333	8.000			
4	78.13	0.3972	3.667	7.333	11.000			
5	82.33	0.4333	4.000	8.000	12.000			
6	98.93	0.5776	5.333	10.665	15.998			
7	111.83	0.6859	6.333	12.665	18.998			
8	116.36	0.7220	6.666	13.331	19.997			

Worked Example cont…

Step 5: Compare results with the sequences of $h^2 + k^2 + l^2$ values to identify the Bravais lattice.

Peak No.	2θ	$\sin^2\theta$	$1\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$2\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$3\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$h^2+k^2+l^2$	hkl	a (Å)
1	38.43	0.1083	1.000	2.000	3.000	3	111	4.0538
2	44.67	0.1444	1.333	2.667	4.000	4	200	4.0539
3	65.02	0.2888	2.667	5.333	8.000	8	220	4.0538
4	78.13	0.3972	3.667	7.333	11.000	11	311	4.0538
5	82.33	0.4333	4.000	8.000	12.000	12	222	4.0538
6	98.93	0.5776	5.333	10.665	15.998	16	400	4.0541
7	111.83	0.6859	6.333	12.665	18.998	19	331	4.0540
8	116.36	0.7220	6.666	13.331	19.997	20	420	4.0541

Bravais lattice is Face-Centered Cubic

$$\sin^2\theta = \left(\frac{\lambda^2}{4a^2}\right)\left(h^2 + k^2 + l^2\right)$$

Worked Example cont…

Step 6: Calculate lattice parameters

Peak No.	2θ	$\sin^2\theta$	$1\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$2\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$3\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$h^2+k^2+l^2$	hkl	a (Å)
1	38.43	0.1083	1.000	2.000	3.000	3	111	4.0538
2	44.67	0.1444	1.333	2.667	4.000	4	200	4.0539
3	65.02	0.2888	2.667	5.333	8.000	8	220	4.0538
4	78.13	0.3972	3.667	7.333	11.000	11	311	4.0538
5	82.33	0.4333	4.000	8.000	12.000	12	222	4.0538
6	98.93	0.5776	5.333	10.665	15.998	16	400	4.0541
7	111.83	0.6859	6.333	12.665	18.998	19	331	4.0540
8	116.36	0.7220	6.666	13.331	19.997	20	420	4.0541

Average lattice parameter is 4.0539 Å

Analytical

Recall: $\sin^2\theta = \left(\frac{\lambda^2}{4a^2}\right)\left(h^2 + k^2 + l^2\right)$ and $\left(\frac{\lambda^2}{4a^2}\right)$ = constant for all patterns

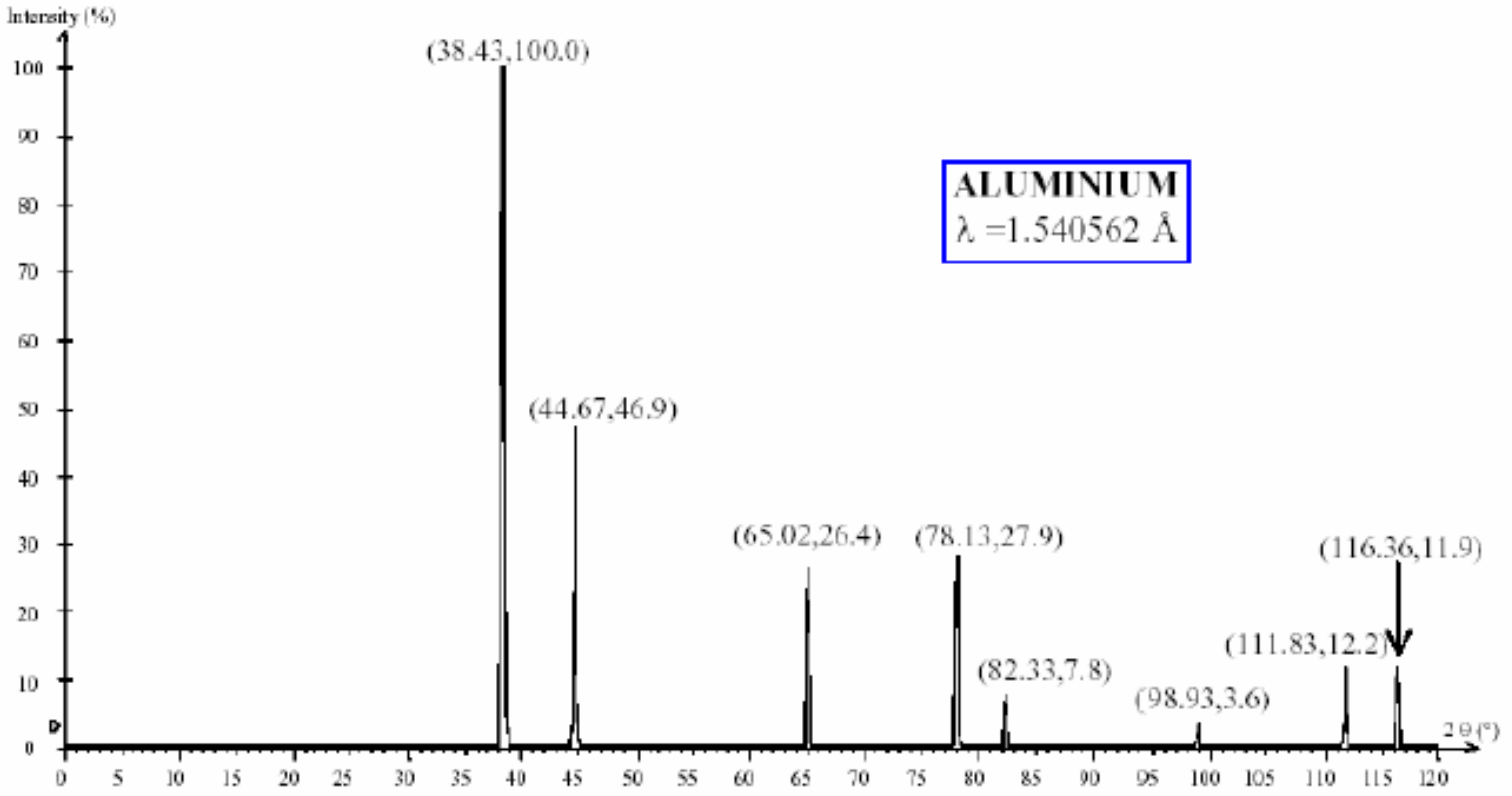
Let $K = \frac{\lambda^2}{4a^2}$ then $\sin^2\theta = K\left(h^2 + k^2 + l^2\right)$

For any cubic system, $h^2 + k^2 + l^2$ = 1,2,3,4,5,6,8,9,10,11,12,…

If we determine $\sin^2\theta$ for each peak and divide the values by the integers 2,3,4,5,6,8,9,10,11…, we can obtain a common quotient, which is the value of K

Worked Example

Consider the following XRD pattern for Aluminum, which was collected using CuKα radiation.



Index this pattern and determine the lattice parameters.

Worked Example cont…

Steps:

(1) Identify the peaks.

(2) Determine $\sin^2\theta$

(3) Calculate the ratio $\sin^2\theta$/(integers) $\sin^2\theta = K\left(h^2 + k^2 + l^2\right)$

(4) Identify the lowest common quotient from (3) and identify the integers to which it corresponds. Let the lowest common quotient be *K*.

(5) Divide $\sin^2\theta$ by *K* for each peak. This will give you a list of integers corresponding to $h^2 + k^2 + l^2$

(6) Select the appropriate pattern of $h^2 + k^2 + l^2$ values and identify the Bravais lattice.

(7) Calculate lattice parameters.

Worked Example cont…

(1) Identify the peaks.

Peak No.	2θ	$\sin^2\theta$	$\frac{\sin^2\theta}{2}$	$\frac{\sin^2\theta}{3}$	$\frac{\sin^2\theta}{4}$	$\frac{\sin^2\theta}{5}$	$\frac{\sin^2\theta}{6}$	$\frac{\sin^2\theta}{8}$
1	38.43							
2	44.67							
3	65.02							
4	78.13							
5	82.33							
6	98.93							
7	111.83							
8	116.36							

Worked Example cont…

(2) Determine $\sin^2\theta$.

Peak No.	2θ	$\sin^2\theta$	$\frac{\sin^2\theta}{2}$	$\frac{\sin^2\theta}{3}$	$\frac{\sin^2\theta}{4}$	$\frac{\sin^2\theta}{5}$	$\frac{\sin^2\theta}{6}$	$\frac{\sin^2\theta}{8}$
1	38.43	0.1083						
2	44.67	0.1444						
3	65.02	0.2888						
4	78.13	0.3972						
5	82.33	0.4333						
6	98.93	0.5776						
7	111.83	0.6859						
8	116.36	0.7220						

Worked Example cont…

(3) Calculate the ratio $\sin^2\theta$ /(integers)

Peak No.	2θ	$\sin^2\theta$	$\frac{\sin^2\theta}{2}$	$\frac{\sin^2\theta}{3}$	$\frac{\sin^2\theta}{4}$	$\frac{\sin^2\theta}{5}$	$\frac{\sin^2\theta}{6}$	$\frac{\sin^2\theta}{8}$
1	38.43	0.1083	0.0542	0.0361	0.0271	0.0217	0.0181	0.0135
2	44.67	0.1444	0.0722	0.0481	0.0361	0.0289	0.0241	0.0181
3	65.02	0.2888	0.1444	0.0963	0.0722	0.0578	0.0481	0.0361
4	78.13	0.3972	0.1986	0.1324	0.0993	0.0794	0.0662	0.0496
5	82.33	0.4333	0.2166	0.1444	0.1083	0.0867	0.0722	0.0542
6	98.93	0.5776	0.2888	0.1925	0.1444	0.1155	0.0963	0.0722
7	111.83	0.6859	0.3430	0.2286	0.1715	0.1372	0.1143	0.0857
8	116.36	0.7220	0.3610	0.2407	0.1805	0.1444	0.1203	0.0903

Worked Example cont…

(4) Identify the lowest common quotient from (3) and identify the integers to which it corresponds. Let the lowest common quotient be K.

Peak No.	2θ	$\sin^2\theta$	$\frac{\sin^2\theta}{2}$	$\frac{\sin^2\theta}{3}$	$\frac{\sin^2\theta}{4}$	$\frac{\sin^2\theta}{5}$	$\frac{\sin^2\theta}{6}$	$\frac{\sin^2\theta}{8}$
1	38.43	0.1083	0.0542	**0.0361**	0.0271	0.0217	0.0181	0.0135
2	44.67	0.1444	0.0722	0.0481	**0.0361**	0.0289	0.0241	0.0181
3	65.02	0.2888	0.1444	0.0963	0.0722	0.0578	0.0481	**0.0361**
4	78.13	0.3972	0.1986	0.1324	0.0993	0.0794	0.0662	0.0496
5	82.33	0.4333	0.2166	0.1444	0.1083	0.0867	0.0722	0.0542
6	98.93	0.5776	0.2888	0.1925	0.1444	0.1155	0.0963	0.0722
7	111.83	0.6859	0.3430	0.2286	0.1715	0.1372	0.1143	0.0857
8	116.36	0.7220	0.3610	0.2407	0.1805	0.1444	0.1203	0.0903

$K = 0.0361$

Worked Example cont…

(5) Divide $\sin^2\theta$ by K for each peak. This will give you a list of integers corresponding to $h^2+k^2+l^2$.

Peak No.	2θ	$\sin^2\theta$	$\frac{\sin^2\theta}{K}$	$h^2+k^2+l^2$	hkl
1	38.43	0.1083	3.000		
2	44.67	0.1444	4.000		
3	65.02	0.2888	8.001		
4	78.13	0.3972	11.001		
5	82.33	0.4333	12.002		
6	98.93	0.5776	16.000		
7	111.83	0.6859	19.001		
8	116.36	0.7220	20.000		

Worked Example cont…

(6) Select the appropriate pattern of $h^2 + k^2 + l^2$ values and identify the Bravais lattice.

Peak No.	2θ	$\sin^2\theta$	$\frac{\sin^2\theta}{K}$	$h^2 + k^2 + l^2$	hkl
1	38.43	0.1083	3.000	3	111
2	44.67	0.1444	4.000	4	200
3	65.02	0.2888	8.001	8	220
4	78.13	0.3972	11.001	11	311
5	82.33	0.4333	12.002	12	222
6	98.93	0.5776	16.000	16	400
7	111.83	0.6859	19.001	19	331
8	116.36	0.7220	20.000	20	420

Sequence suggests a Face-Centered Cubic Bravais Lattice

(7) Calculate lattice parameters.

$$a = \frac{\lambda}{2\sqrt{K}} = \frac{1.540562\ \text{Å}}{2\sqrt{0.0361}} = 4.0541\ \text{Å}$$

PART2:
INDEXING A DIFFRACTION PATTERN FROM NON-CUBIC MATERIALS

Mathematical

- Consider the plane spacing equations for the crystal structures of interest.

Hexagonal $$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$$

Tetragonal $$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad (1)$$

Orthorhombic $$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Etc.

- Recall Bragg's law: $\lambda = 2d \sin\theta$

$$\lambda^2 = 4d^2 \sin^2\theta \text{ OR } \sin^2\theta = \frac{\lambda^2}{4d^2} \quad (2)$$

Mathematical cont..

- Combining Eqn. (1) and (2) yields

Hexagonal $$\frac{1}{d^2}=\frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right)+\frac{l^2}{c^2}=\frac{4\sin^2\theta}{\lambda^2}$$

Tetragonal $$\frac{1}{d^2}=\frac{h^2+k^2}{a^2}+\frac{l^2}{c^2}=\frac{4\sin^2\theta}{\lambda^2}$$

Orthorhombic $$\frac{1}{d^2}=\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}=\frac{4\sin^2\theta}{\lambda^2}$$

Etc…

- Which can be rearranged in terms of $\sin^2\theta$ as

Hexagonal $$\sin^2\theta=\left(\frac{\lambda^2}{4}\right)*\left[\frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right)+\frac{l^2}{c^2}\right]$$

Tetragonal $$\sin^2\theta=\left(\frac{\lambda^2}{4}\right)\left(\frac{h^2+k^2}{a^2}+\frac{l^2}{c^2}\right)$$

Orthorhombic $$\sin^2\theta=\left(\frac{\lambda^2}{4}\right)\left(\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}\right)$$

Tetragonal System

In this system, the $\sin^2\theta$ values obey the following relation:

$$\sin^2\theta = A\,(h^2 + k^2) + Cl^2$$

where A (= $\lambda^2/4a^2$) and C (= $\lambda^2/4c^2$) are constants for any pattern.

First of all these constants (A and C) are found which will then disclose the cell parameters a and c and enable the line indices to be calculated. The value of A is obtained from the $hk0$ lines. When l = 0 the above equation becomes:

$$\sin^2\theta = A\,(h^2 + k^2)$$

The permissible values of ($h^2 + k^2$) are 1, 2, 4, 5, 8, etc. Therefore the $hk0$ lines must have $\sin^2\theta$ values in the ratio of these integers and A will be some number which is 1, 1/2, 1/4, 1/5, 1/8, etc., times the $\sin^2\theta$ values of these lines. C is obtained from the other lines on the pattern and by the use of the following equation.

$$\sin^2\theta - A\,(h^2 + k^2) = Cl^2$$

Differences represented by the left-hand side of the equation are set up, for various assumed values of h and k, in an attempt to find a consistent set of Cl^2 values, which must be in the ratio of 1, 4, 9, 16, etc. Once these values are found, C can be calculated.

Autoindexing

- **Manual indexing of cubic unit cells is a reasonably straightforward process.**
- **Tetragonal, trigonal and hexagonal cells can also be indexed manually with some experience, but it is not a trivial exercise.**
- **Generally indexing is done using a computer program. This process is called autoindexing.**
- **The input for an autoindexing program is typically:**
  - **The peak positions (ideally 20-30 lines)**
  - **The wavelength**
  - **The uncertainty in the peak positions**
  - **The maximum allowable unit cell volume**

Autoindexing Software

A number of the most useful autoindexing programs have been gathered together by Robin Shirley into a single package called *Crysfire*. You can download Crysfire from the web and find tutorials on its use at

http://www.ccp14.ac.uk/tutorial/crys/index.html

To index a powder diffraction pattern try the following steps:

- **Fit the peaks using a program such as X-Fit (http://www.ccp14.ac.uk/tutorial/xfit-95/xfit.htm)**
- **Take the X-fit output file and convert to a Crysfire input file, as described on the web.**
- **Run Crysfire to look for the best solutions.**
- **Evaluate the systematic absences and refine the cell parameters. This can be done using the material in the front of the international tables for crystallography or using a program like Chekcell (http://www.ccp14.ac.uk/tutorial/lmgp/index.html).**

Autoindexing - Pitfalls

- Inaccurate data
- Impurities
  - Try different programs
  - Drop out various weak peaks
  - Try different sample preps
  - Complimentary analysis
- Psuedosymmetry
  - Unit cell dimensions are close to a more symmetric crystal system
- Inadequate number of peaks
  - You really need 15-25 peaks, particularly if the symmetry is low

How do I know when I'm finished?

- Evaluate output based on figure of merit, when the following conditions are met the solution warrants close consideration
  - $M_{20} > 10$
  - All of the peaks are indexed
- Solutions with figures of merit above 20 or so almost always have some degree of the truth in them, but closely related solutions and partially correct solutions are common.
- Favor high symmetry solutions over low symmetry ones.

Determination of Number of Atoms in a Unit Cell

In structure determination process, the next step after establishing the shape and size of the unit cell is to find the number of atoms in the unit cell, because the number of atoms must be known before their positions can be determined.

When the unit cell volume, calculated from the lattice parameters, is multiplied by the measured density of the substance it gives the weight of all the atoms in the cell.

$$\sum A = \rho \frac{V}{1.66042}$$

Where $\sum A$ **is the sum of the atomic weights of the atoms in the unit cell,** ρ **is the density (g/cm^3) and *V* is the volume of the unit cell (Å^3). If the substance is an element of atomic weight *A*, then**

$$\sum A = n_1 A$$

Where *n1* is the number of atoms per unit cell. If the substance is a chemical compound then

$$\sum A = n_2 M$$

Where *n2* is the number of molecules per unit cell and *M* the molecular weight. The number of atoms per unit cell can then be calculated from *n2* and the composition of the phase.

Volume of the Unit Cell

The following equations are used to calculate the volume *V* of the unit cell:

Cubic:	$V = a^3$
Tetragonal:	$V = a^2c$
Orthorhombic:	$V = abc$
Monoclinic:	$V = abc \sin\beta$
Hexagonal:	$V = 0.866a^2c$