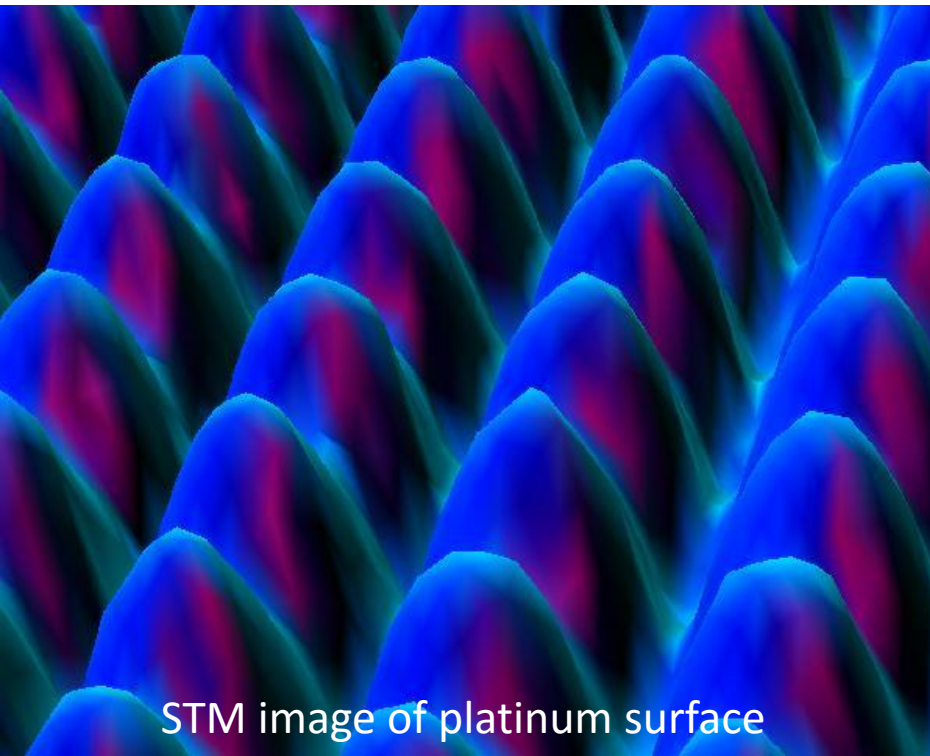


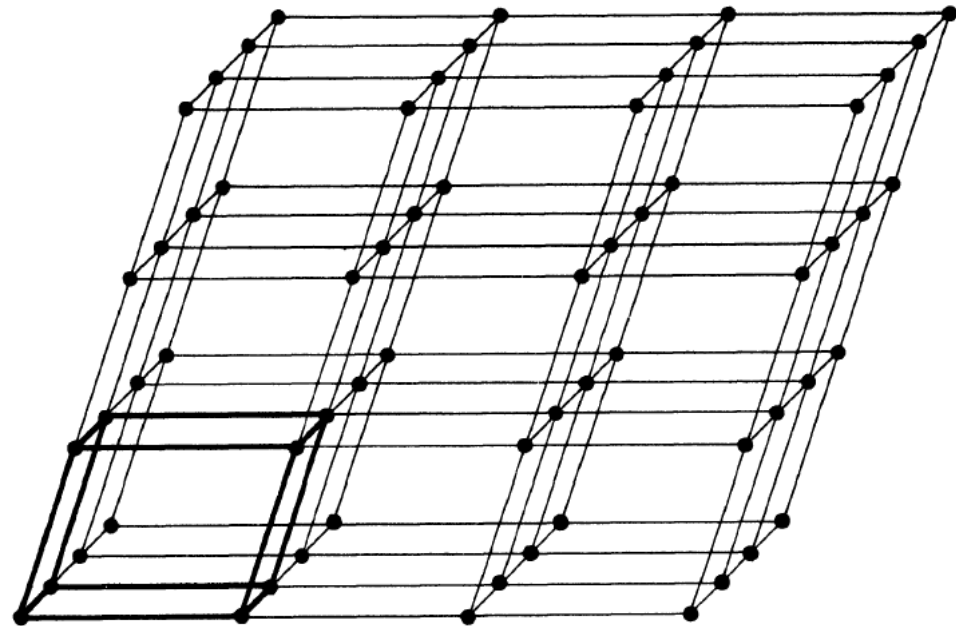
# X-ray Techniques for Crystallinity Analysis

# Crystalline Materials

- Crystal is defined as a solid composed of atoms arranged in a pattern that is periodic in three dimensions
- All solid metals and ceramics have regular, repeating arrangements of atoms or molecules



STM image of platinum surface



Point lattice



# Haüy's Theory: Molecules

## Matter Theory: 2 Stage Molecular Model

Compound determinately-shaped polyhedral *molécules intégrantes* built out of **Elementary *molécules constituantes*** whose shapes are not inferable

## Crystal Structure Theory: 2 Stage

**Core: Primitive form**, constant and common to crystals of same species, revealed by **cleavage**

**Secondary (external) forms:** Derived from primitive form by **decrements (recessions)** in each successive layer of *molécules intégrantes* by **small integer number of molecules**.

# Haüy's Theory: Crystal Structure

Haüy's molecular structural models

*Traité de Minéralogie*

(1801). Fig. 13 & 16:

**cubic** *molécules intégrantes*,

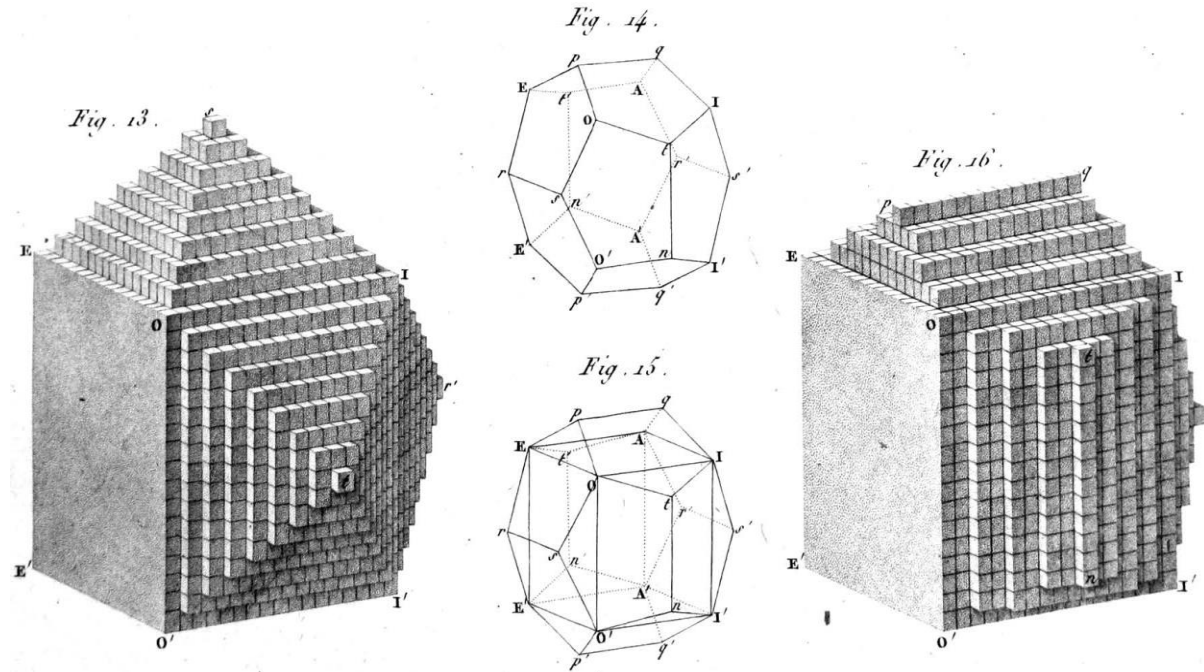
**cubic** *primitive form*

**simple decrement**

rhomb-dodecahedron (Fig. 13)

**complex decrements**

pentagon-dodecahedron (Fig. 16)



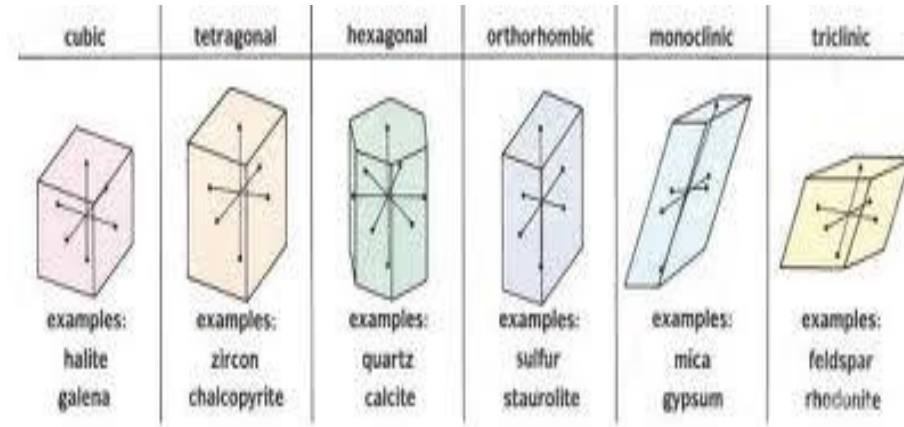
# Crystalline Symmetry & Systems

The over-riding focus in 19<sup>th</sup>-century crystallography: abstract, mathematical considerations of **crystalline symmetry**.

This was initiated early in the 19<sup>th</sup> century in Germany by **Christian Samuel Weiss**, (1780 – 1856) who **preferred molecule models of crystal structure in favor of more dynamical ones, relating to axes of symmetry**.

Influence of German **Naturphilosophie**.

Monoclinic & triclinic systems identified by **Friedrich Mohs**. Subsequently, the hexagonal system was divided into the trigonal and hexagonal, making 7 systems.



# Auguste Bravais (1811 -1863)

Bravais, a graduate of the **École Polytechnique** and a professor of physics, worked out a *mathematical theory of crystal symmetry* based on the concept of the **crystal lattice, of which there were 14.**



# Crystallography After Bravais

During the remainder of the 19<sup>th</sup> century, the basis for modern crystal structure theory was development on the basis of Bravais's formulation of crystal lattices.

**These developments were largely mathematical and had little concern with the actual interpretation of atomic and molecular arrangement.**



# X-Ray Diffraction: April, 1912

Von Laue designed an experiment in which he placed a copper sulphate crystal between an X-ray tube and a photographic plate. His assistants, **Walther Friedrich and Paul Knipping**, carried out the experiment. After a few initial failures, they met with success on **23 April, 1912**. X-rays passing through the crystal formed the pattern of bright spots that proved the hypothesis was correct.”

[http://www.nobelprize.org/nobel\\_prizes/physics/laureates/1914/perspectives.html](http://www.nobelprize.org/nobel_prizes/physics/laureates/1914/perspectives.html)

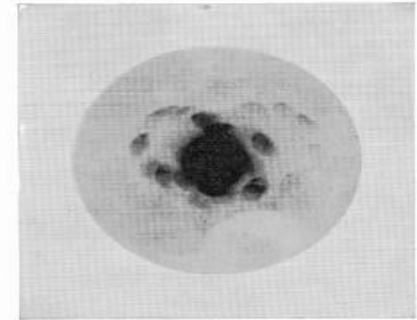


Fig. 4-4(1). Friedrich & Knipping's first successful diffraction photograph.

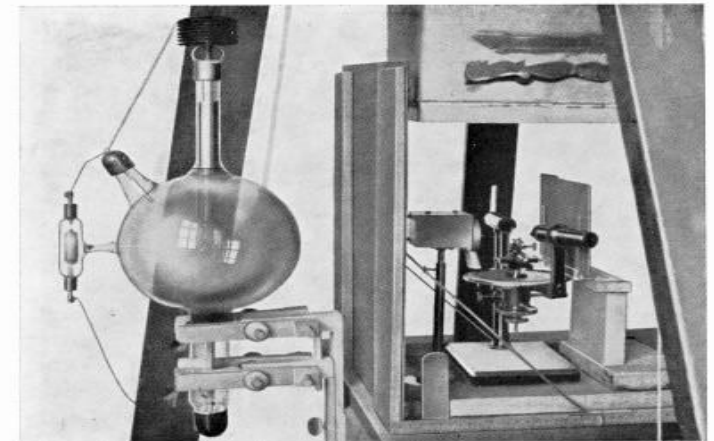


Fig. 4-4(2). Friedrich & Knipping's improved set-up.

# Von Laue to Braggs

“Regarding the explanation, **Laue** thinks it is due to the diffraction of the röntgen rays by the regular structure of the crystal....**He is, however, at present unable to explain the phenomenon in its detail.**’\* ...

Once back in Cambridge, W. L. Bragg continued to pour over the Laue results, and **recalled...the crystal structure theories of William Pope and William Barlow.** He became convinced that the effect was optical and visualized an explanation in terms of the simple reflection of X-rays from the planes of atoms in the crystal.

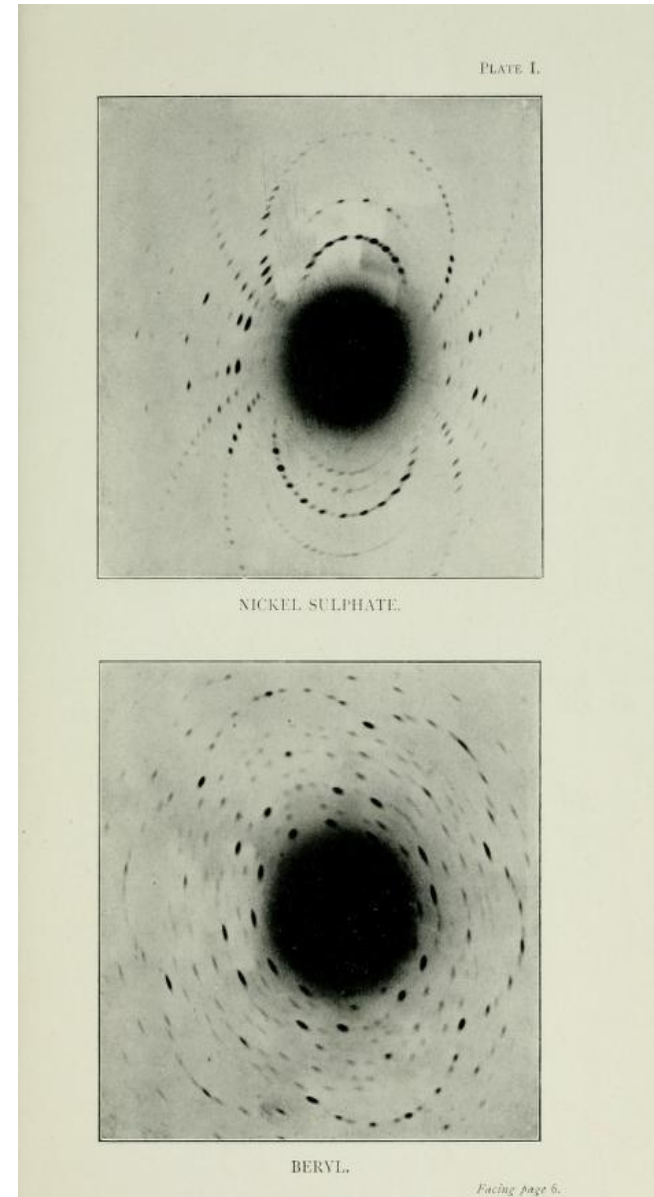
He thereby devised **Bragg’s Law.,  $n\lambda=2d\sin\theta$ .**”

\* Letter, Lars Vegard – W.H. Bragg, June 26, 1912. John Jenkins, “A Unique Partnership: William and Lawrence Bragg and the 1915 Nobel Prize in Physics,” *Minerva*, 2001, Vol. 39, No. 4, pp. 380-381.

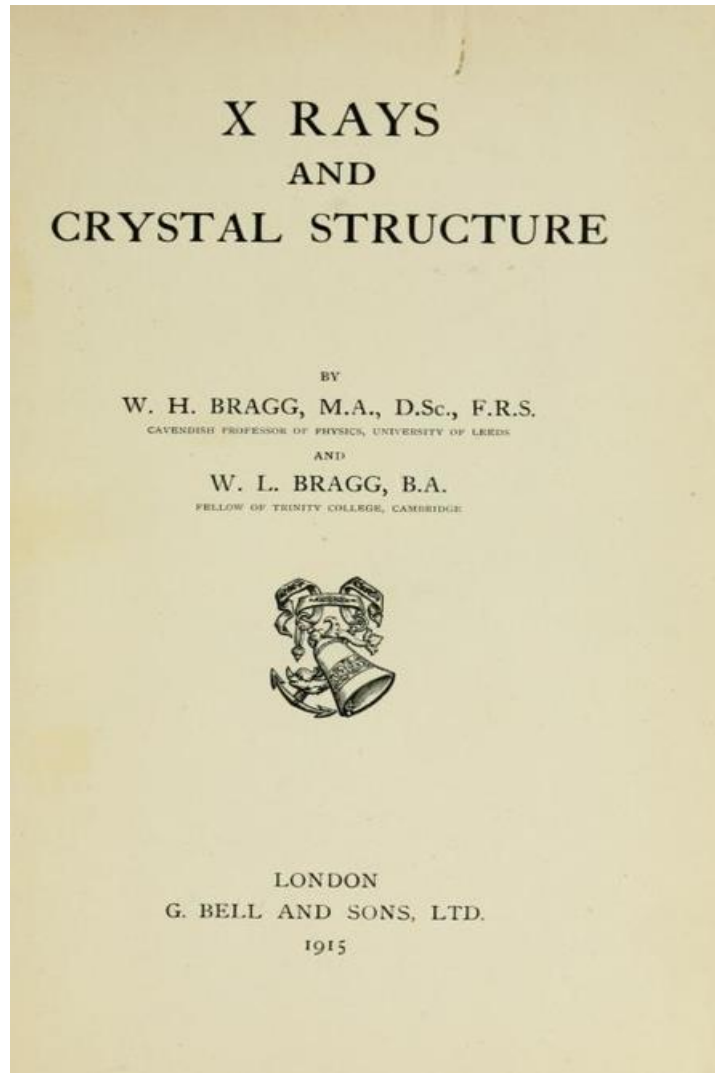
## W.H. & W. L. Bragg, X-Rays and Crystal Structure (1915)

“It is natural to suppose that the Laue pattern owes its origin to the interference of waves diffracted at a number of centres which are closely connected with the atoms or molecules of which the crystal is built, and are therefore arranged according to the same plan.

**The crystal is, in fact, acting as a diffraction grating.”** (pp. 8-9).



# W. H. & W. L. Bragg, *X-Rays and Crystal Structure* (1915)



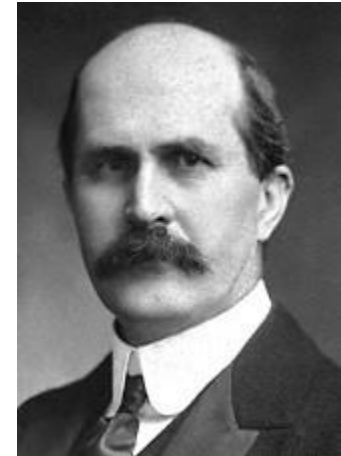
Photos

Top: William Henry Bragg  
(1862 – 1942);

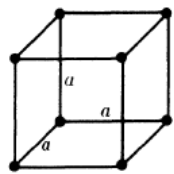
Bottom William Lawrence  
Bragg

(1890-1971)

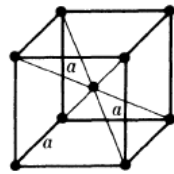
Swedish postage stamp  
with Braggs



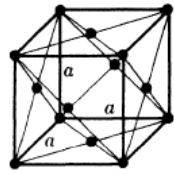
# Geometry of Crystals



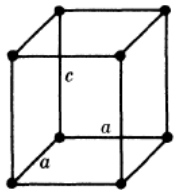
SIMPLE  
CUBIC (P)



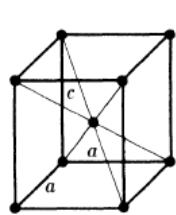
BODY-CENTERED  
CUBIC (I)



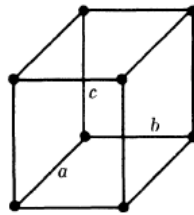
FACE-CENTERED  
CUBIC (F)



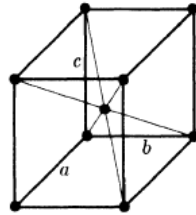
SIMPLE  
TETRAGONAL  
(P)



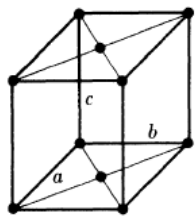
BODY-CENTERED  
TETRAGONAL  
(I)



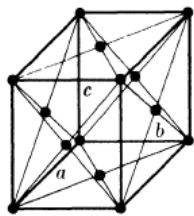
SIMPLE  
ORTHORHOMBIC  
(P)



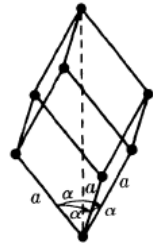
BODY-CENTERED  
ORTHORHOMBIC  
(I)



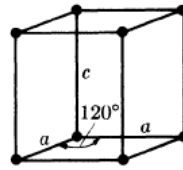
BASE-CENTERED  
ORTHORHOMBIC  
(C)



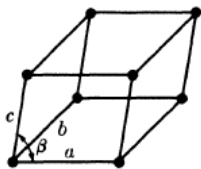
FACE-CENTERED  
ORTHORHOMBIC  
(F)



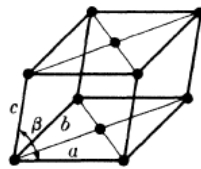
RHOMBOHEDRAL  
(R)



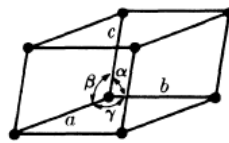
HEXAGONAL  
(P)



SIMPLE  
MONOCLINIC (P)



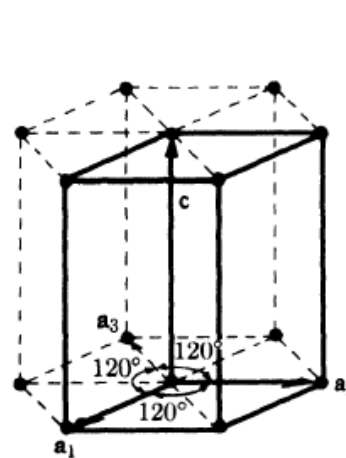
BASE-CENTERED  
MONOCLINIC (C)



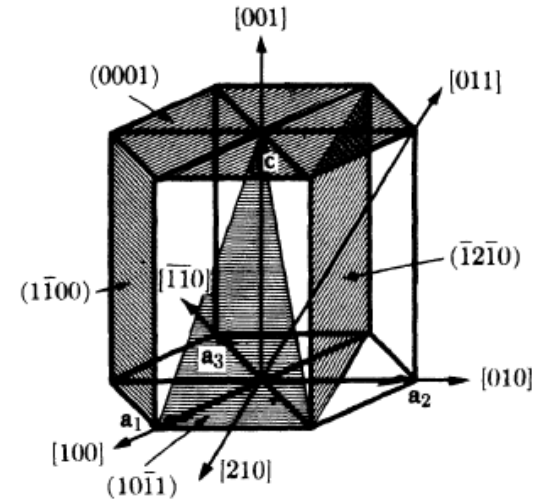
TRICLINIC (P)

14 point lattices found in nature

- Unit cell is the basic repeating unit that defines a crystal
- Parallel planes of atoms intersecting the unit cell are used to define directions and distances in the crystal
- Each diffraction peak is produced by a family of atomic planes.



(a)



(b)

The hexagonal unit cell (a), and indices of planes and directions (b)

Figures adapted from Chapter 2 – The Geometry of Crystals of ``Elements of X-Ray Diffraction`` by Cullity

# LATTICE ARRAYS AND BRAVAIS LATTICES

**Crystalline materials** differ from amorphous materials in that in the former there is order in the arrangement of the molecular contents whereas in the latter there is no order or a tendency for a short-range order.

**The packing of atoms, molecules or ions** within a crystal occurs in a symmetrical manner and furthermore this symmetrical arrangement is repetitive.

The most important common characteristic that crystals may share is the manner in which repetition occurs. This is expressed in a common lattice array.

**A lattice array** is constructed from the arrangement of atomic material within the crystal

## A 2-dimensional Lattice

Pick any position within the 2 dimensional lattice in Fig. 1(a) and note the arrangement about this point. The chosen position can be indicated by a point (a lattice point). In view of the repetitive arrangement, there will be a 2 dimensional array of identical positions and if these are also marked by a point a 2-dimensional lattice will result if the points are joined.

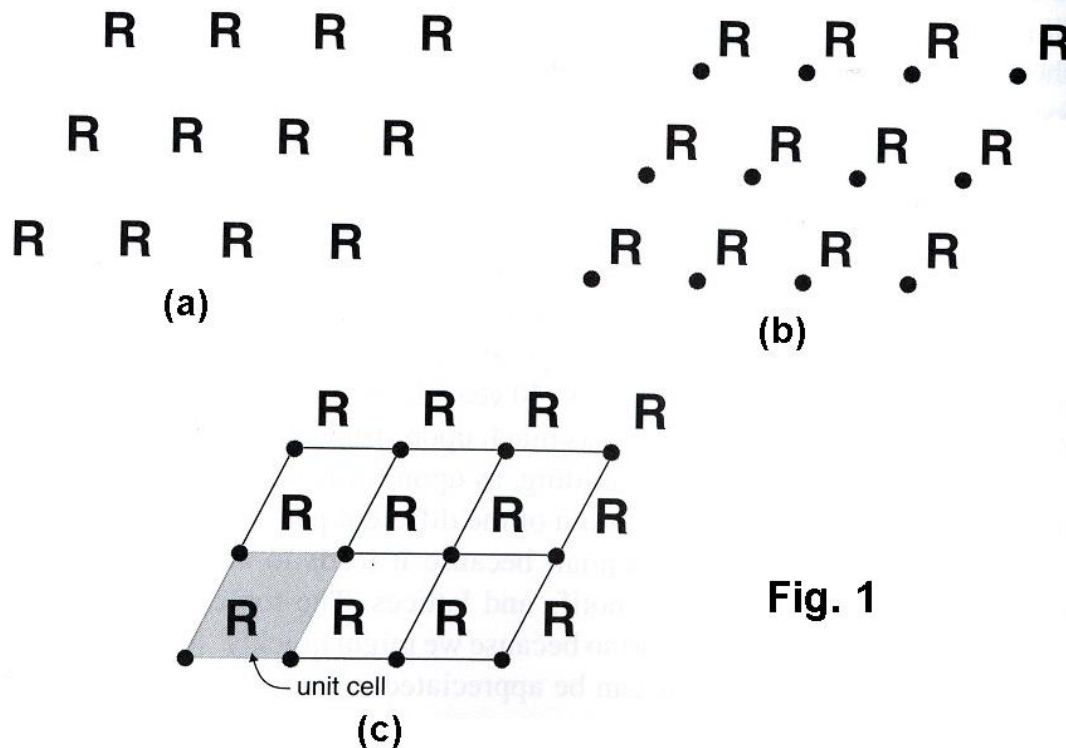


Fig. 1

## In a real 3-dimensional crystal lattice the same ideas apply.

When crystal structures are represented by lattices, it transpires that all crystals break down into one of fourteen three dimensional lattice arrangements.

**Bravais** demonstrated mathematically that there are only fourteen ways in which repetitive symmetry can occur and the fourteen lattices representing the ways in which repetition can occur are referred to as the **Bravais** lattices.

### UNIT CELL

A unit cell can be any unit of a lattice array which when repeated in all directions, and *always maintaining the same orientation in space*, generates the lattice array.

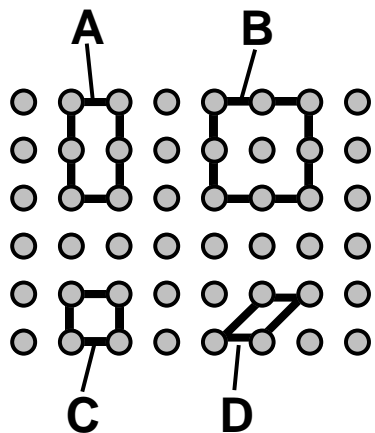


Fig. 2

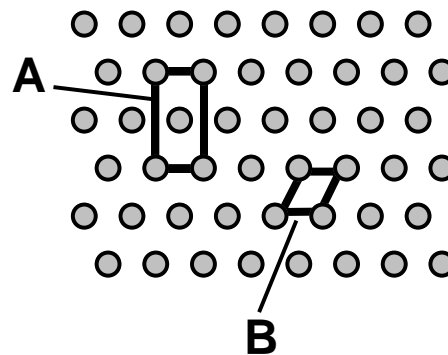


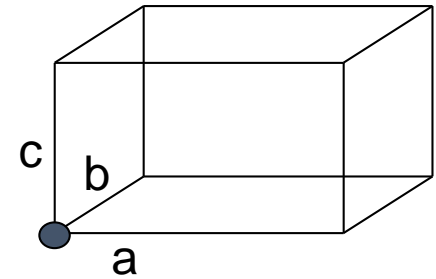
Fig. 3

There is no unique way of choosing a unit cell. For example, each of the cells (**A** to **D**) in Fig. 2 are OK. However, the cell favoured by crystallographers is the one of smallest volume that displays all of the symmetry of the lattice. Thus, cells **C** and **A** are the preferred unit cells for the lattices of Figs. 2 and 3 respectively.

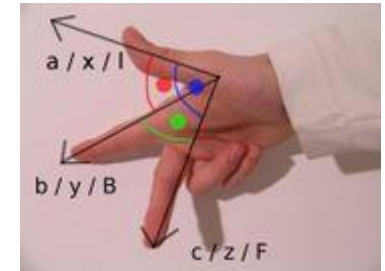


## UNIT CELL TYPES and THE SEVEN CRYSTAL SYSTEMS

Cubic	$a = b = c.$	$\alpha = \beta = \gamma = 90^\circ.$
Tetragonal	$a = b \neq c.$	$\alpha = \beta = \gamma = 90^\circ.$
Orthorhombic	$a \neq b \neq c.$	$\alpha = \beta = \gamma = 90^\circ.$
Monoclinic	$a \neq b \neq c.$	$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ.$
Triclinic	$a \neq b \neq c..$	$\alpha \neq \beta \neq \gamma \neq 90^\circ.$
Rhombohedral (or Trigonal)	$a = b = c.$	$\alpha = \beta = \gamma \neq 90^\circ.$
Hexagonal	$a = b \neq c.$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ.$



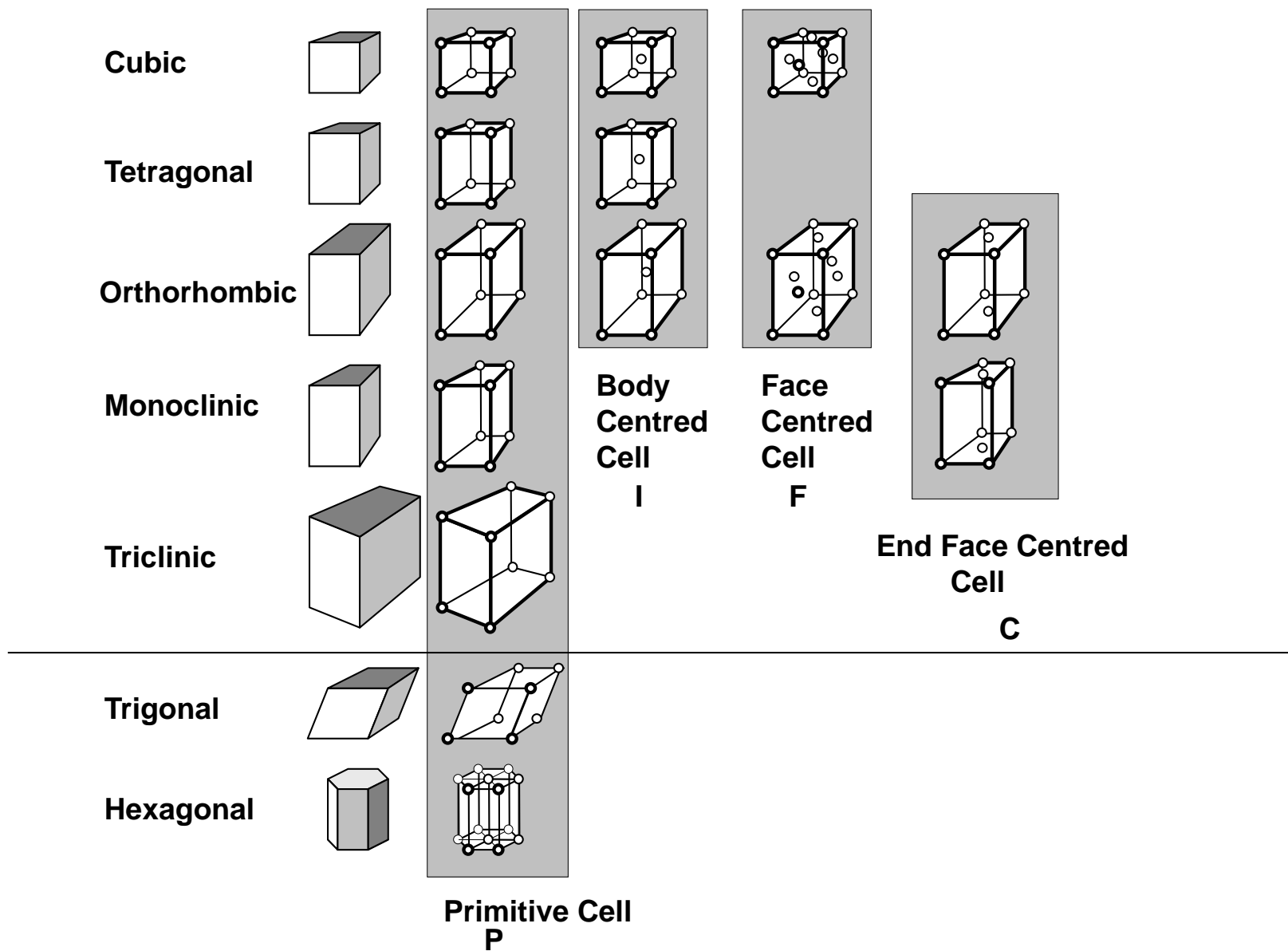
Orthorhombic



In general, six parameters are required to define the shape and size of a unit cell, these being three cell edge lengths (conventionally, defined as  $a$ ,  $b$ , and  $c$ ), and three angles (conventionally, defined as  $\alpha$ ,  $\beta$ , and  $\gamma$ ). In the strict mathematical sense,  $a$ ,  $b$ , and  $c$  are vectors since they specify both length and direction.

$\alpha$  is the angle between  $b$  and  $c$ ,  $\beta$  is the angle between  $a$  and  $c$ ,  $\gamma$  is the angle between  $a$  and  $b$ . The unit cell should be right handed. Check the cell above with your right hand

When these unit cells are combined with possible “centering” there are 14 different Bravais lattices.



**Fig. 3**

## Four simple points on crystal lattices:

1. Every crystal system has a primitive Bravais lattice.
2. The distribution of lattice points in a cell must be such as to maintain the total symmetry of the crystal system.  
Thus, the cubic system cannot have a **C**-type cell.
3. The fact that a unit cell meets the symmetry requirements of a crystal system does not guarantee its inclusion within the crystal system. This could result if the lattice it generated could be equally well represented by a unit cell type which is already included within the crystal system. The C-type cell for the tetragonal system (see Fig. 4) provides a good example.

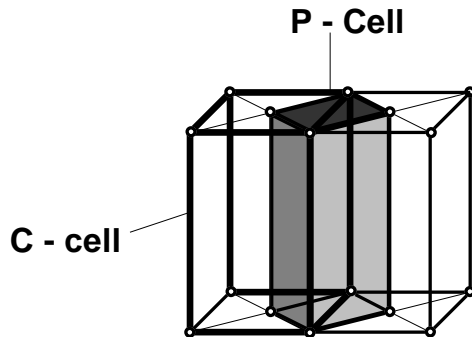


Fig. 4

4. If you repeat 3. within the orthorhombic system you will find that the primitive cell you generate will not have  $90^\circ$  angles. This is not orthorhombic and thus orthorhombic C is included in the crystal system.

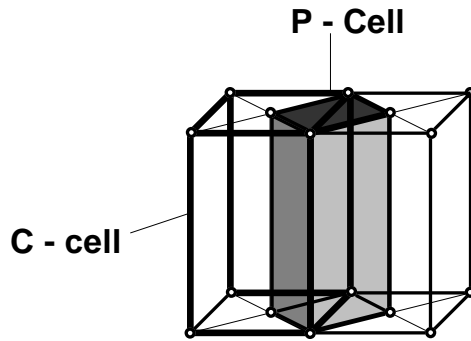
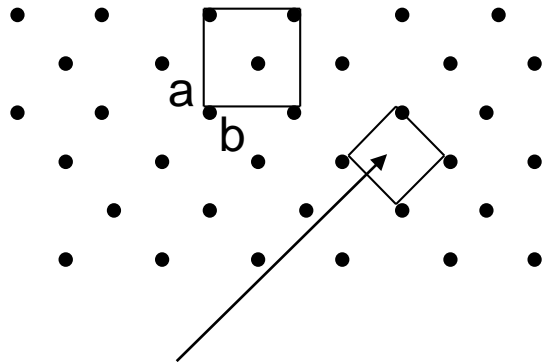


Fig. 4

A simplified view down c-axis can be used to illustrate points 3 and 4

Tetragonal

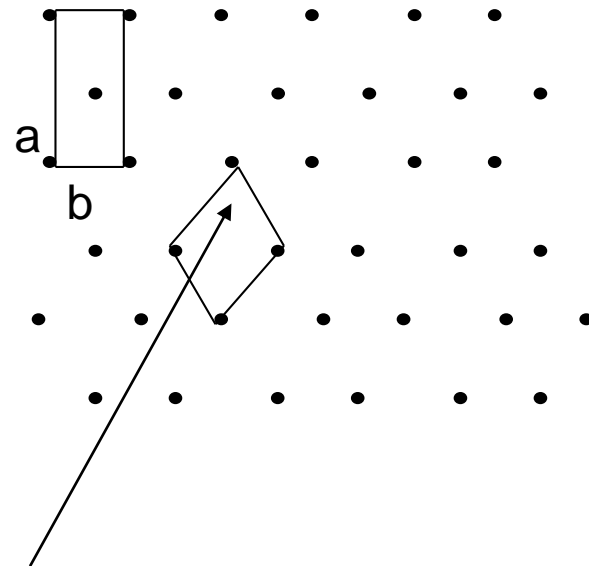
$$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$$



Smaller cell is Tetragonal P

Orthorhombic

$$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$$



Angle not  $90^\circ$  smaller cell  
not orthorhombic

# SYMMETRY: POINT GROUP SYMMETRY AND SPACE GROUP SYMMETRY

Point group theory is not our scope. What follows is just a summary.

Point group symmetry defines the symmetry of an isolated object or group of objects, whereas space group symmetry further defines the systematic fashion in which an object, or group of objects is repeated in space to generate an infinite periodic array in 3D.

Point group symmetry is quantified in terms of symmetry elements (existing within the object or group of objects) and their associated operations. Four symmetry elements are used to quantify point group symmetry

## **Symmetry Element**

Rotation axis (n-fold)

Mirror plane

Centre of Symmetry

Rotor-reflection axis (n-fold)

or

Rotor-inversion axis (n-fold)

## **Symmetry Operation**

Rotation

Reflection

Inversion

Rotation and reflection

Rotation and inversion

# Symmetry Elements and Operations

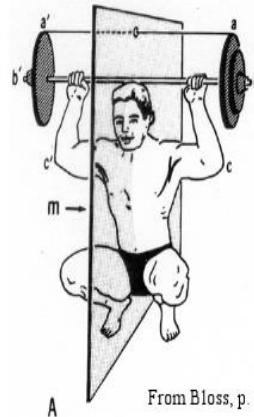
***“Symmetry elements*** define the (conceptual) motion of an object in space the carrying out of which, the ***symmetry operation***, leads to an arrangement that is indistinguishable from the initial arrangement.”

Werner Massa, *Crystal Structure Determination* (2004), p. 41.

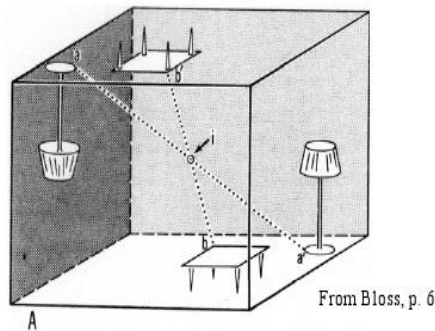
# Symmetry Operations ---} 32 Point Groups

## Rotation, reflection and inversion

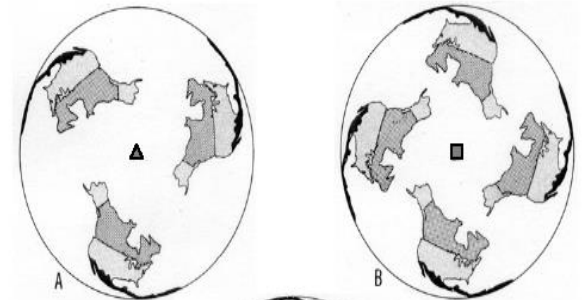
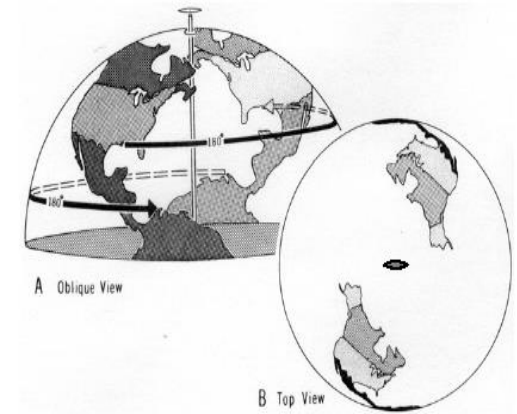
operations  
generate a variety  
of unique  
arrangements of  
lattice points (i.e.,  
a shape structure)  
in three  
dimensions.



2. REFLECTION =  $m$



4. INVERSION =  $i$



From Bloss, pp. 4, 5

$$\alpha = 360^\circ/n$$

$n$  = fold of axis = 1, 2, 3, 4 or 6

3. ROTATION

# Point Group and Space Group Symmetry

To generate a 3D lattice from an object it is necessary to add translational symmetry to point group symmetry. The two important space group symmetry operations which move objects are glide planes and screw axes. These operations combine translation and reflection and translation and rotation respectively.

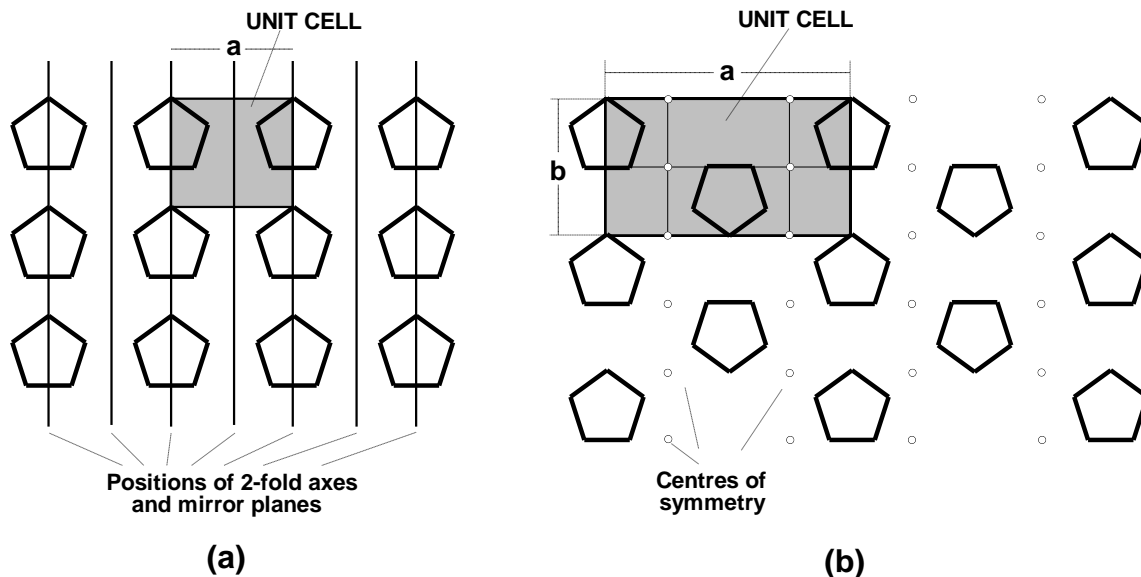


Fig. 5

The pentagons on the left are related by simple translation. In 5(b) the pentagon on the top left of the cell is related to the one in the centre by translation  $a/2$  followed by either reflection or rotation. Centres of inversion in 5(b) are marked with tiny circles.



## The 230 Space Groups

There is an infinite number of combinations of the four symmetry elements. ***However, if there is a restriction on the order of the rotation axes to 2, 3, 4, and 6, as is the case for repetitive symmetry (crystallographic symmetry) this leaves only 32 unique combinations. These are the 32 crystallographic point groups. Adding screw axes and glide planes gives the 230 space groups.*** The overall breakdown of symmetry for crystals then is as shown in Fig. 9.

CRYSTAL SYSTEMS (7)	BRAVAIS LATTICES (14)	SPACE GROUPS (230)
Cubic	P	15
	F	11
	I	10
		36
Tetragonal	P	49
	I	19
		68
Orthorhombic	P	30
	F	5
	I	9
	C and A	15
		59
Monoclinic	P	8
	C	5
		13
Triclinic	P	2
Rhombohedral	P and R	25
Hexagonal	P	27

The International Tables for Crystallography list the symmetry properties for all 230 Space Groups. The 2<sup>nd</sup> edition was in one volume and edited by Kathleen Lonsdale. The current edition runs to 7 volumes. The CSD or Cambridge Data Base is a repository for the structures of organic and organometallic compounds.

Space Group determination is an important step in crystal structure determination.

Fig. 9

# CRYSTAL PLANES AND MILLER INDICES

The use of crystal planes to describe the structure of crystals goes back to the start of crystallography and crystal planes were used by Bragg to explain diffraction as will be seen later.

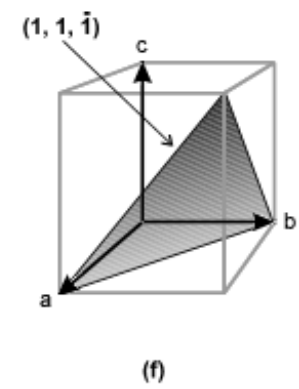
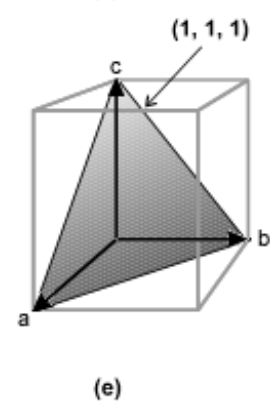
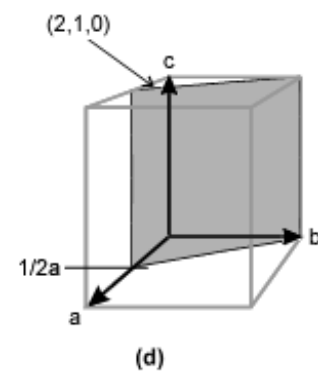
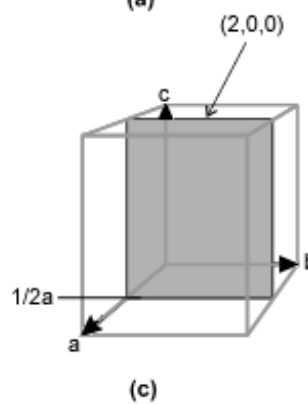
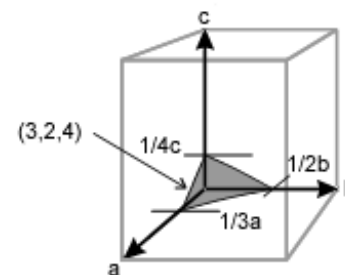
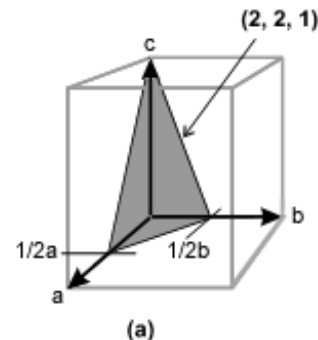
Crystal planes are defined by the intercepts they make on the crystal axes of the unit cell.

The inverse of these fractions are the Miller Indices of the planes.

In (a) the intercepts are  $\frac{1}{2}$ ,  $\frac{1}{2}$ , 1 and the Miller Indices are (2 2 1).

In (c) the intercepts on b and c are at infinity the inverse of which is 0 and the plane is the (2 0 0).

In (f) the plane cuts the negative c axis at -1 and thus is (1 1  $\bar{1}$ ). In crystallography -1 is often written  $\bar{1}$  and pronounced “Bar 1”.



# DIFFRACTION AND THE BRAGG EQUATION

Max von Laue was the first to suggest that crystals might diffract X-rays and he also provided the first explanation for the diffraction observed. However, it is the explanation provided by Bragg that is simpler and more popular.

In the Bragg view, crystal planes act as mirrors. Constructive interference is observed when the path difference between the two reflected beams in (a)  $= n\lambda$ . The path difference in (a) is  $2my$ . Since  $my/d = \sin\theta$   
 $2my = 2d\sin\theta = n\lambda$   
 where  $d$  is the interplanar spacing.

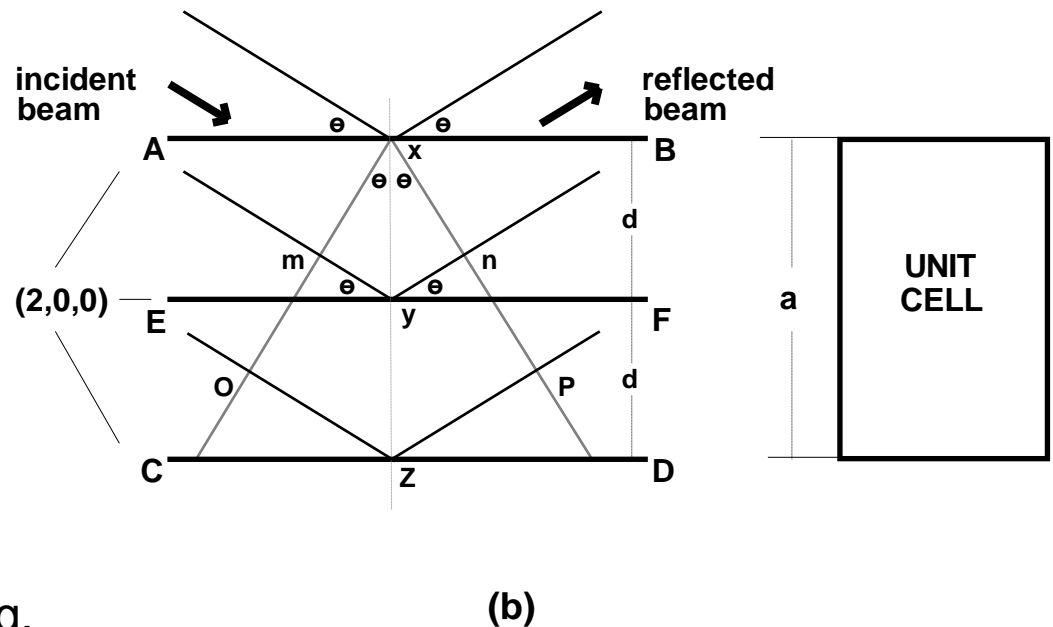
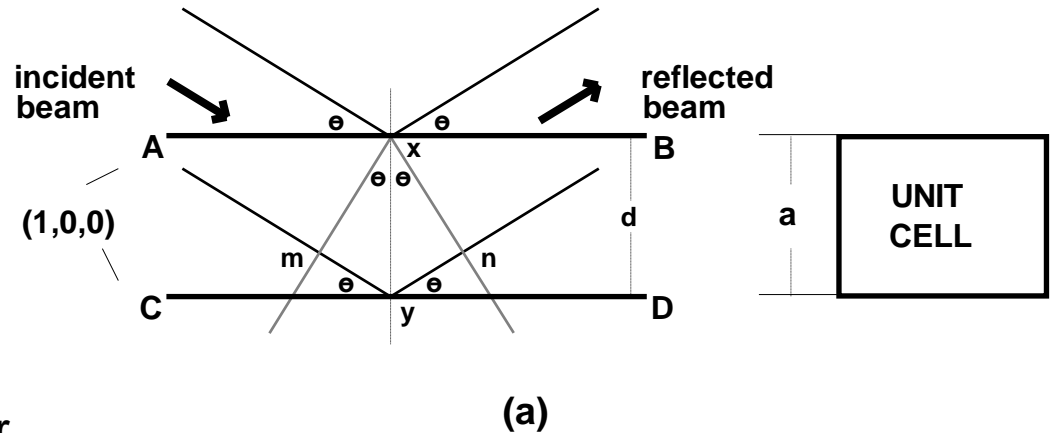


Fig. 11

In (a) it is clear that the planes are the (1,0,0) set of planes.  
If the path difference is simply one wavelength the Bragg condition can be stated as

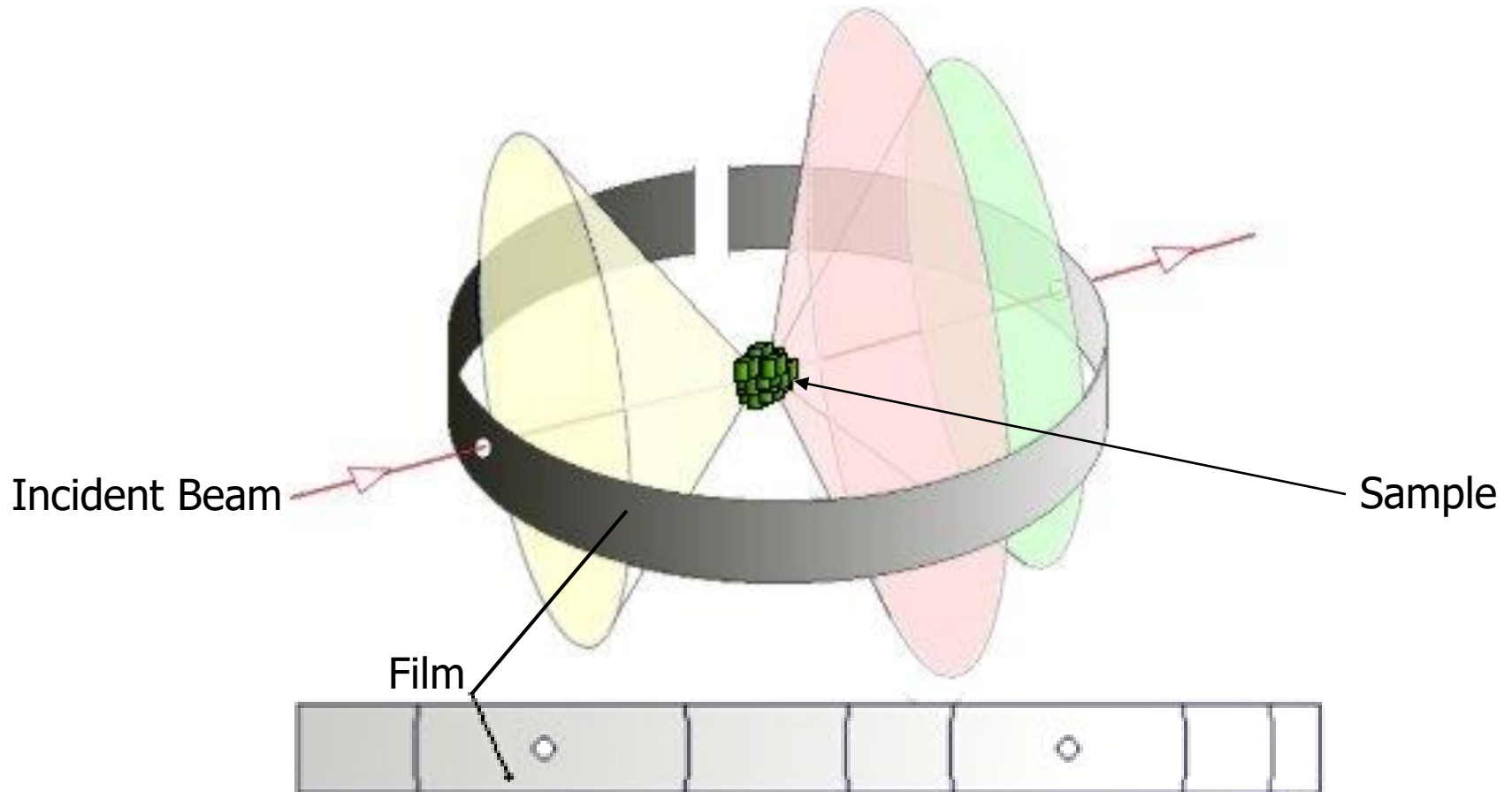
$$2d_{(1,0,0)} \sin \theta = \lambda$$

This is a ***first order reflection***. If the path difference is two wave lengths the Bragg condition becomes

$$2d_{(1,0,0)} \sin \theta = 2\lambda$$

and the reflection is a ***second order reflection***.

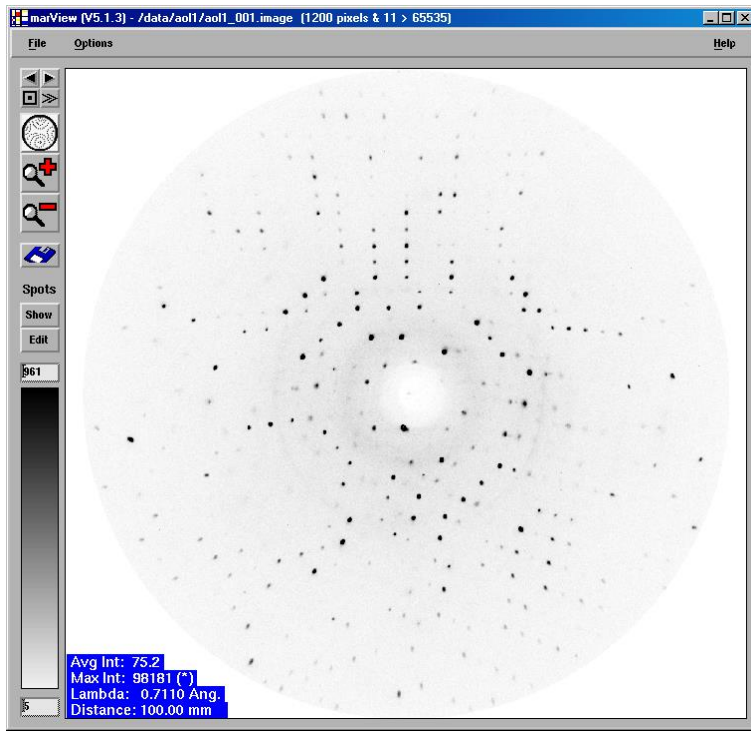
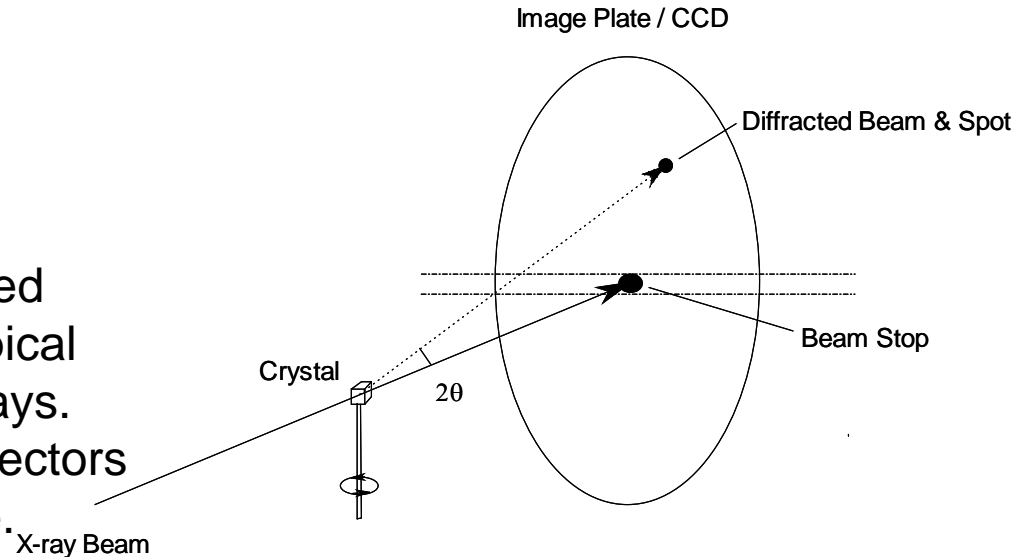
# Powder Method



- Useful for determining lattice parameters with high precision and for identification of phases

# Diagram Of An Area Detector X-Ray Data Collection System.

The first crystallographic data collection systems used photographic methods. These were replaced by automated diffractometers which measured reflections one at a time. A typical data collection took several days. modern systems use area detectors which measure 100s at a time.



The crystal is oscillated over  $< 2^\circ$  while an image is collected then rotated by the same amount and oscillated again. The process is repeated over a total range of about  $180^\circ$ . Each image is exposed for  $< 100$ s. Thus if readout time is ignored total data collection time is often  $< 3$  hr. A typical image shown to the left. A computer program is used to predict the unit cell from several images.

# SOLVING A CRYSTAL STRUCTURE BY SINGLE CRYSTAL DIFFRACTION TECHNIQUES

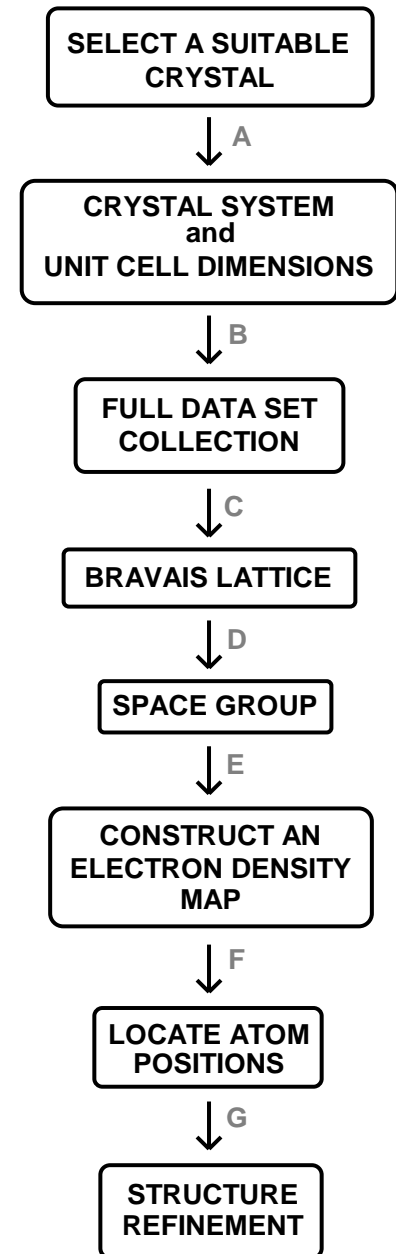
**The crystal must be a single crystal.**

Bragg's equation specifies that, if a crystal is rotated within a monochromatic X-ray beam, such that every conceivable orientation of the crystal relative to the beam is achieved, each set of planes will have had the opportunity to satisfy the Bragg equation and will have given rise to reflection.

In order to solve a crystal structure it is necessary to record a large number of reflections.

This implies accurately measuring their intensities and recording their directions with respect to crystal orientation and initial X-ray beam direction.

Many experimental techniques have been devised to achieve this. The steps involved in a crystal structure determination are summarised in the flow chart.



## Determination of the Lattice type and Space Group

High symmetry can lead to reflections being systematically absent from the data set. Absent reflections have no measurable intensity. There are two types of absences, **General Absences** and **Special Absences**.

The general absences determine the lattice type;

Primitive (**P**) has no general absences and no restrictions on  $h$ ,  $k$  or  $l$ .

End Centered (**C**)  $h+k=2n+1$  are all absent.

Face Centered (**F**) only  $h$ ,  $k$ ,  $l$ , all even or all odd are observed.

Body Centered (**I**)  $h+k+l=2n+1$  are all absent.

The special absences refer to specific sets of reflections and are used to detect the presence of glide planes and screw axes. Some Space Groups are uniquely determined by special absences but in many cases several Space Groups will have to be considered.



# Structure Factor

$$F_{hkl} = \sum_1^N f_n e^{2\pi i(hu_n + kv_n + lw_n)}$$

Intensity of the diffracted beam  $\propto |F|^2$

- $h, k, l$ : indices of the diffraction plane under consideration
- $u, v, w$ : co-ordinates of the atoms in the lattice
- $N$ : number of atoms
- $f_n$ : scattering factor of a particular type of atom

Bravais Lattice	Reflections possibly present	Reflections necessarily absent
Simple	All	None
Body Centered	$(h+k+l)$ : Even	$(h+k+l)$ : Odd
Face Centered	$h, k,$ and $l$ unmixed i.e. all odd or all even	$h, k,$ and $l$ : mixed

# Systematic Absences

## Permitted Reflections

Simple Cubic	$(100), (110), (111), (200), (210), (211),$ $(220), (300), (221) \dots\dots\dots$
BCC	$(110), (200), (211), (220), (310), (222) \dots\dots$
FCC	$(111), (200), (220), (311) \dots\dots$

## Calculations using X-ray powder diffraction patterns

For an orthogonal system ( $\alpha = \beta = \gamma = 90^\circ$ ) the relationship between interplanar spacing ( $d$ ) and the unit cell parameters is given by the expression:

$$\frac{1}{d_{(h,k,l)}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

This is the expression for an orthorhombic crystal.

For the tetragonal system it reduces to

$$\frac{1}{d_{(h,k,l)}^2} = \frac{(h^2 + k^2)}{a^2} + \frac{l^2}{c^2}$$

and, for the cubic system, it further reduces to

$$\frac{1}{d_{(h,k,l)}^2} = \frac{(h^2 + k^2 + l^2)}{a^2}$$

# Phase Identification based on Lattice Parameter Determination

- Complete determination of an unknown crystal structure is possible by
  1. Calculation of the size and shape of the unit cell from the angular positions of the diffraction peaks
  2. Computation of the number of atoms per unit cell from the size and shape of the unit cell, the chemical composition of the specimen, and its measured density
  3. Deduction of the atom positions within the unit cell from the relative intensities of the diffraction peaks

The first step is indexing pattern – assigning Miller indices to each peak

$$d_{hkl} = \frac{a_o}{\sqrt{h^2 + k^2 + l^2}} \quad \text{Cubic unit cell}$$

Bragg's law becomes

$$\lambda^2 = 4d^2 \sin^2 \theta = \frac{4a_o^2}{(h^2 + k^2 + l^2)} \sin^2 \theta$$

The Bragg equation may be rearranged (if  $n=1$ )

from  $n\lambda = 2d \sin \theta$  to  $\frac{\lambda^2}{4d^2} = \sin^2 \theta$

If the value of  $1/(d_{h,k,l})^2$  in the cubic system equation above is inserted into this form of the Bragg equation you have

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

Since in any specific case  $a$  and  $\lambda$  are constant and if  $\lambda^2/4a^2 = A$

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

# Phase Identification based on Lattice Parameter Determination

- In the cubic system, the first reflection in the diffraction pattern is due to diffraction from planes with Miller indices (100) for primitive cubic, (110) for body-centered cubic, and (111) for face-centered cubic lattices, so  $h^2 + k^2 + l^2 = 1, 2, \text{ or } 3$ , respectively

$$\frac{\sin^2 \theta}{(h^2 + k^2 + l^2)} = \frac{\sin^2 \theta}{s} = \frac{\lambda^2}{4a_0^2}$$

← constant for a given crystal

always equal to an integer

Comparing the observed integer values of the peaks with the characteristic line sequences in the cubic system

Simple cubic: 1, 2, 3, 4, 5, 6, 8, 9, 10, 11, 12, 13, 14, 16, ...

Body-centered cubic: 2, 4, 6, 8, 10, 12, 14, 16, ...

Face-centered cubic: 3, 4, 8, 11, 12, 16, 19, 20, 24, 27, 32, ...

Diamond cubic: 3, 8, 11, 16, 19, 24, 27, 32, ...

Calculate the average lattice parameter by least squares method

# Phase Identification based on Lattice Parameter Determination

Example for an FCC material

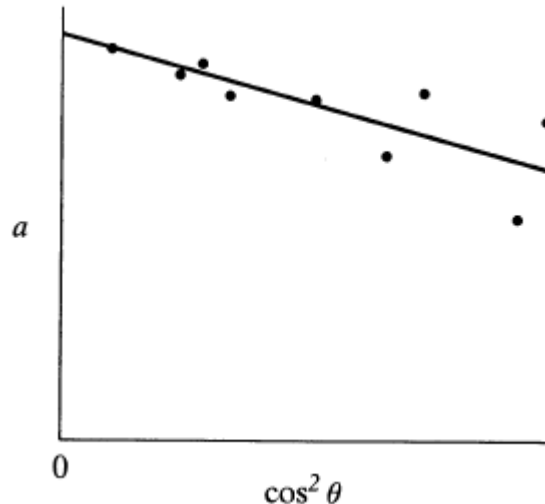
1	2	3	4	5	6	7	8	9	10
FCC						SC		BCC	
Line	$\sin^2 \theta$	$s = (h^2 + k^2 + l^2)$	$\frac{\sin^2 \theta}{s} = \frac{\lambda^2}{4a^2}$	$a(\text{\AA})$	$hkl$	$s$	$\frac{\sin^2 \theta}{s}$	$s$	$\frac{\sin^2 \theta}{s}$
1	0.140	3	0.0467	3.57	111	1	0.140	2	0.0700
2	0.185	4	0.0463	3.59	200	2	0.093	4	0.0463
3	0.369	8	0.0461	3.59	220	3	0.123	6	0.0615
4	0.503	11	0.0457	3.61	311	4	0.123	8	0.0629
5	0.548	12	0.0457	3.61	222	5	0.110	10	0.0548
6	0.726	16	0.0454	3.62	400	6	0.121	12	0.0605
7	0.861	19	0.0453	3.62	331	8	0.108	14	0.0615
8	0.905	20	0.0453	3.62	420	9	0.101	16	0.0566

# Lattice Parameter Determination

- Calculation of the lattice parameter from one peak is prone to error due to
  - Displacement of the specimen from the diffractometer axis
  - Misalignment of the instrument
  - Use of a flat specimen instead of a specimen curved to conform to the focusing circle
  - Absorption in the specimen
  - Vertical divergence of the incident beam

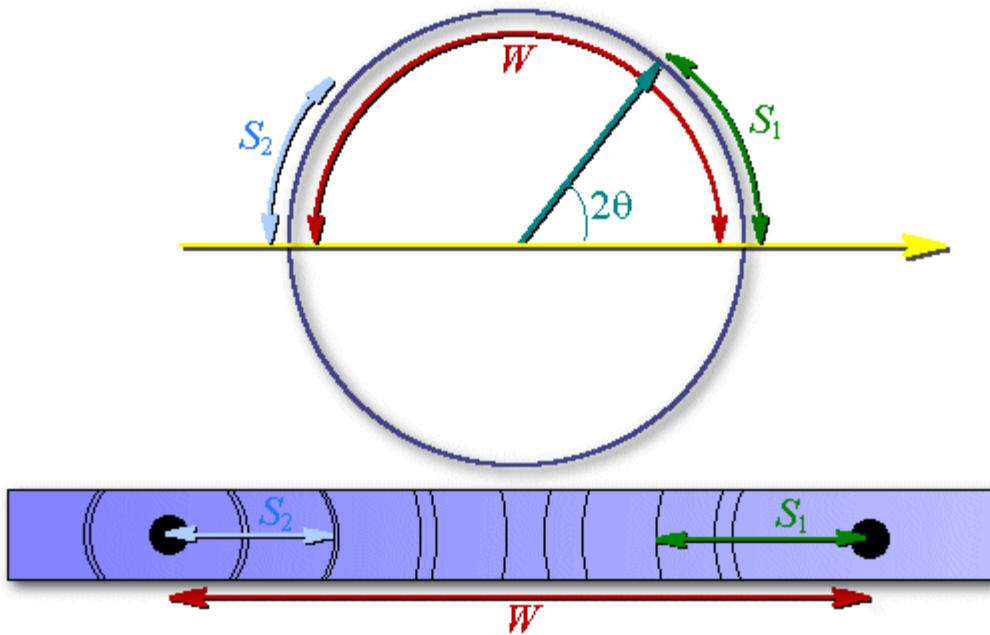
These errors cause  $\Delta d/d$  to be approximately proportional to  $\cos^2\theta$

Accurate lattice parameter value can be obtained by simple extrapolation against  $\cos^2\theta$  using the least squares method





# Indexing a Laue powder pattern



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

For cubic crystals

$$d_{hkl} = \frac{a_o}{\sqrt{h^2 + k^2 + l^2}}$$

$$\theta = \frac{\pi S_1}{2W} \text{ (for front reflections) or}$$

$$\theta = \frac{\pi}{2} \left( 1 - \frac{S_2}{W} \right) \text{ (for back reflections)}$$

$$\lambda^2 = 4d^2 \sin^2 \theta = \frac{4a_o^2}{(h^2 + k^2 + l^2)} \sin^2 \theta$$

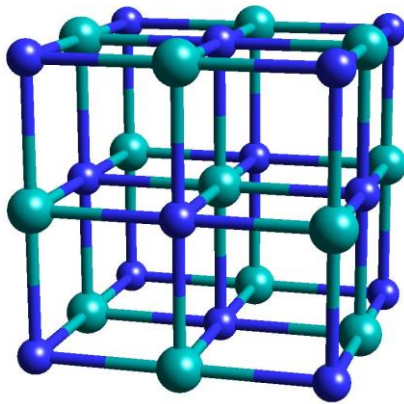
# Indexing

FCC; wavelength=1.54056Å					
$S_1$ (mm)	$\theta(^{\circ})$	$\sin^2\theta$	$h^2+k^2+l^2$	$\sin^2\theta / h^2+k^2+l^2$	Lattice Parameter, a (Å)
38	19.0	0.11	3	0.037	4.023
45	22.5	0.15	4	0.038	3.978
66	33.0	0.30	8	0.038	3.978
78	39.0	0.40	11	0.036	4.039
83	41.5	0.45	12	0.038	3.978
97	49.5	0.58	16	0.036	4.046
113	56.5	0.70	19	0.037	4.023
118	59.0	0.73	20	0.037	4.023
139	69.5	0.88	24	0.037	4.023
168	84.9	0.99	27	0.037	4.023
				<b>Constant; so it is FCC</b>	

# Important Cubic Lattice Types

Two of the most important cubic lattice types are the NaCl type and the CsCl type.

NaCl crystallizes in the Space Group **Fm-3m**



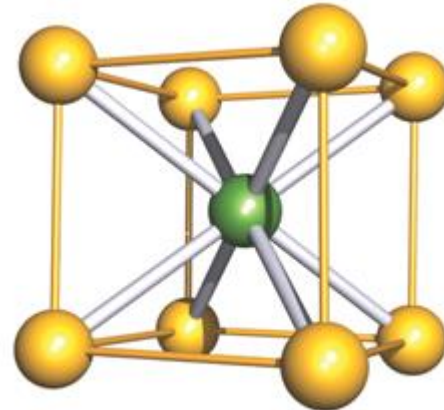
Stoichiometry (formula) from the Unit Cell

Site	Na <sup>+</sup>	Cl <sup>-</sup>
Central	0	1
Face	6/2	0
Edge	0	12/4
Corner	8/8	0
Total	4	4

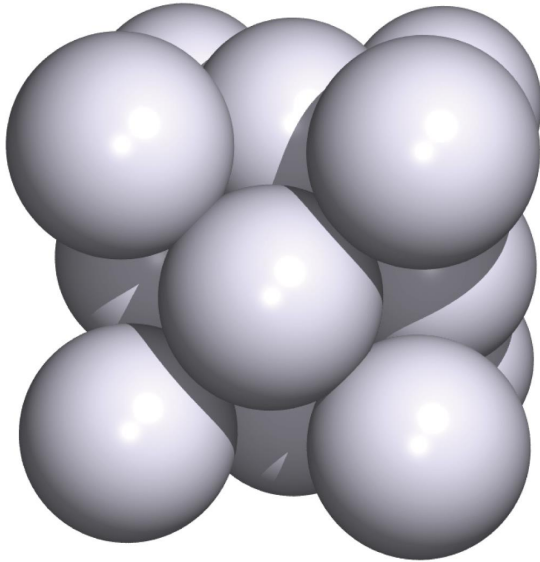
In the CsCl structure both ions have coordination numbers of 8 and the structure is a simple primitive

Formula Cs at centre = 1

$$8 \times 1/8 \text{Cl} = 1 = \text{CsCl}$$



## Cubic close packed spheres



The unit cell of a cubic close packed metal has a face centered or **F** type lattice

The formula of the unit cell is:

$$6 \times \frac{1}{2} + 8 \times \frac{1}{8} = 4$$

**Name and formula**

Reference code: 00-001-1260

PDF index name: Nickel

Empirical formula: Ni

Chemical formula: Ni

**Crystallographic parameters**

Crystal system: Cubic

Space group: Fm-3m

Space group number: 225

a (Å): 3.5175

b (Å): 3.5175

c (Å): 3.5175

Alpha (°): 90.0000

Beta (°): 90.0000

Gamma (°): 90.0000

Measured density (g/cm<sup>3</sup>): 8.90

Volume of cell (10<sup>6</sup> pm<sup>3</sup>): 43.52

Z: 4.00

RIR: -

**Status, subfiles and quality**

Status: Marked as deleted by ICDD

Subfiles: Inorganic

Quality: Blank (B)

**References**

Primary reference: Hanawalt et al., *Anal. Chem.*, 10, 475, (1938)

Optical data: *Data on Chem. for Cer. Use, Natl. Res. Council Bull. 107*

Unit cell: *The Structure of Crystals, 1st Ed.*

# ANALYSIS OF X-RAY POWDER DIFFRACTION DATA

Diffraction data have been collected on a powder diffractometer for a series of compounds that crystallise in the cubic system

## Example 1

Aluminium powder gives a diffraction pattern that yields the following eight largest d-spacings: 2.338, 2.024, 1.431, 1.221, 1.169, 1.0124, 0.9289 and 0.9055 Å. Aluminium has a cubic close packed structure and its atomic weight is 26.98 and  $\lambda = 1.5405 \text{ Å}$ .

Index the diffraction data and calculate the density of aluminium.

The Bragg equation,  $\lambda = 2d \sin \theta$  are used to obtain  $\sin \theta$ ,  $\sin \theta = \frac{\lambda}{2d}$

The ccp lattice is an F type lattice and the only reflections observed are those with all even or all odd indices.

Thus the only values of  $\sin^2 \theta$  in  $\sin^2 \theta = A(h^2 + k^2 + l^2)$  that are allowed

are 3A, 4A, 8A, 11A, 12A, 16A and 19A for the first eight reflections.

Insert the values into a table and compute  $\sin\theta$  and  $\sin^2\theta$ .  
 Since the lowest value of  $\sin^2\theta$  is 3A and the next is 4A the first entry in the Calc.  $\sin^2\theta$  column is  $(0.10854/3)*4$  etc.

d/Å	Sin $\theta$	Sin $^2\theta$	Calc. Sin $^2\theta$	(h, k, l)
2.338	0.32945	0.10854		(1,1,1)
2.024	0.38056	0.14482	0.14472	(2,0,0)
1.431	0.53826	0.28972	0.28944	(2,2,0)
1.221	0.63084	0.39795	0.39798	(3,1,1)
1.169	0.65890	0.43414	0.43416	(2,2,2)
1.0124	0.76082	0.57884	0.57888	(4,0,0)
0.9289	0.82921	0.68758	0.68742	(3,3,1)
0.9055	0.85063	0.72358	0.72360	(4,2,0)

The reflections have now been indexed.

## Calculation of a

For the first reflection (for which  $h^2 + k^2 + l^2 = 3$ )

$$\sin^2\theta = 3\lambda^2 / 4a^2$$

$$a^2 = 3\lambda^2 / 4\sin^2\theta$$

$$a = 4.04946 \text{ \AA} = 4.04946 \times 10^{-8} \text{ cm.}$$

## Calculation of the density of aluminium

$$a^3 = 66.40356 \text{ \AA}^3 = 66.40356 \times 10^{-24} \text{ cm}^3.$$

If the density of aluminium is  $\rho$  (g. cm.<sup>-3</sup>), the mass of the unit cell is  
 $\rho \times 66.40356 \times 10^{-24} \text{ g.}$

The unit cell of aluminium contains 4 atoms.

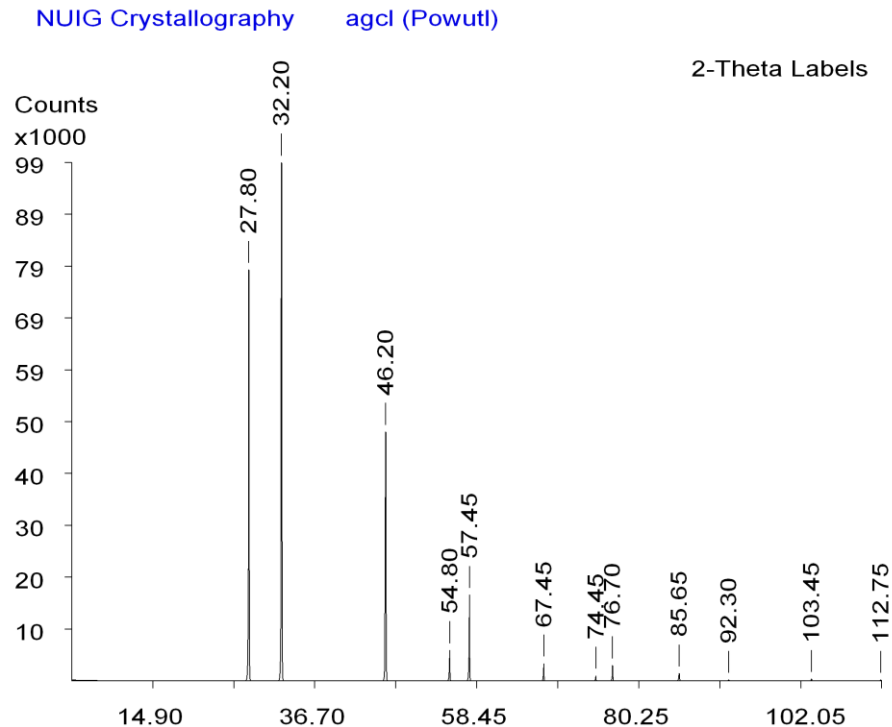
The weight of one aluminium atom is  $26.98 / (6.022 \times 10^{23}) = 4.48024 \times 10^{-23}$   
and the weight of four atoms (the content of the unit cell) is  $179.209 \times 10^{-24}$ .

$$\rho \times 66.40356 \times 10^{-24} = 179.209 \times 10^{-24}$$

$$\rho = 2.6988 \text{ g.cm}^{-3}.$$



Example-2 The X-ray powder diffraction pattern of AgCl obtained using radiation of wavelength  $1.54\text{\AA}$  is shown below. The peaks are labelled with  $2\theta$  values



On the basis that the structure is cubic and of either the NaCl or CsCl type

1. Index the first six reflections.
2. Calculate the unit cell parameter.
3. Calculate the density of AgCl.
4. (Assume the following atomic weights: Ag, 107.868; Cl, 35.453; and Avogadro's number is  $6.022 \times 10^{23}$ )

Since  $\theta$  values are available  $\sin^2\theta$  values can be calculated and inserted in a table.

$2\theta$	$\theta$	$\sin^2\theta$	Calc. $\sin^2\theta$
27.80	13.90	0.0577	
32.20	16.10	0.0769	0.07693
46.20	23.10	0.1539	0.1539
54.80	27.40	0.2118	0.2116
57.45	28.73	0.2310	0.2308
67.45	33.73	0.3083	0.3077

From  $\sin^2\theta = A(h^2 + k^2 + l^2)$  the possible values are:

1. for a face centred lattice 3A, 4A, 8A, 11A, 12A and 16A
2. for a primitive lattice 1A, 2A, 3A, 4A, 5A and 6A

The second option is not possible as the first 2 are not in the ratio of 1:2.  
To test the first option, divide the first by 3 and multiply the result by 4, 8 *etc.*

## Density of AgCl

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

$a^2 = (1.54)^2 \cdot (16) / 4(0.3083)$  using the largest (most accurate)  $2\theta$

$a^2 = 30.7692$

$a = 5.547 \text{ \AA}$  ( $1 \text{ \AA} = 10^{-8} \text{ cm}$ )

Formula wt. of unit cell =  $4\text{AgCl} = 573.284 \text{ g}$

This is the weight of 4 moles of AgCl.

The weight of 4 molecules is  $573.284 / (6.02 \times 10^{23})$

Density =  $573.284 / (6.02 \times 10^{23})(5.547 \times 10^{-8})^3$

A is in  $\text{\AA}$  thus the answer should be multiplied by  $1 / 10^{-24}$

Density =  $5.580 \text{ g/cm}^3$

# General procedure

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

The term in parentheses  $\left( \frac{\lambda^2}{4a^2} \right)$  is constant for any one pattern (because the X-ray wavelength  $\lambda$  and the lattice parameters  $a$  do not change\*). Thus  $\sin^2 \theta$  is proportional to  $h^2 + k^2 + l^2$ . This proportionality shows that planes with higher Miller indices will diffract at higher values of  $\theta$ .

Since  $\left( \frac{\lambda^2}{4a^2} \right)$  is constant for any pattern, we can write the following relationship for any two different planes:

$$\frac{\sin^2 \theta_1}{\sin^2 \theta_2} = \frac{\left( \frac{\lambda^2}{4a^2} \right) (h_1^2 + k_1^2 + l_1^2)}{\left( \frac{\lambda^2}{4a^2} \right) (h_2^2 + k_2^2 + l_2^2)} \text{ or } \frac{\sin^2 \theta_1}{\sin^2 \theta_2} = \frac{(h_1^2 + k_1^2 + l_1^2)}{(h_2^2 + k_2^2 + l_2^2)}.$$

The ratio of  $\sin^2 \theta$  values scales with the ratio of  $h^2 + k^2 + l^2$  values.

In cubic systems, the first XRD peak in the XRD pattern will be due to diffraction from planes with the lowest Miller indices, which interestingly enough are the close packed planes (*i.e.*: simple cubic, (100),  $h^2 + k^2 + l^2 = 1$ ; body-centered cubic, (110)  $h^2 + k^2 + l^2 = 2$ ; and face-centered cubic, (111)  $h^2 + k^2 + l^2 = 3$ ).

Since  $h$ ,  $k$ , and  $l$  are always integers, we can obtain  $h^2 + k^2 + l^2$  values by dividing the  $\sin^2 \theta$  values for the different XRD peaks with the minimum one in the pattern (*i.e.*, the  $\sin^2 \theta$  value from the first XRD peak) and multiplying that ratio by the proper integer (either 1, 2 or 3). This should yield a list of integers that represent the various  $h^2 + k^2 + l^2$  values. You can identify the correct Bravais lattice by recognizing the sequence of allowed reflections for cubic lattices (*i.e.*, the sequence of allowed peaks written in terms of the quadratic form of the Miller indices).

Primitive  $h^2 + k^2 + l^2 = 1, 2, 3, 4, 5, 6, 8, 9, 10, 11, 12, 13, 14, 16 \dots$

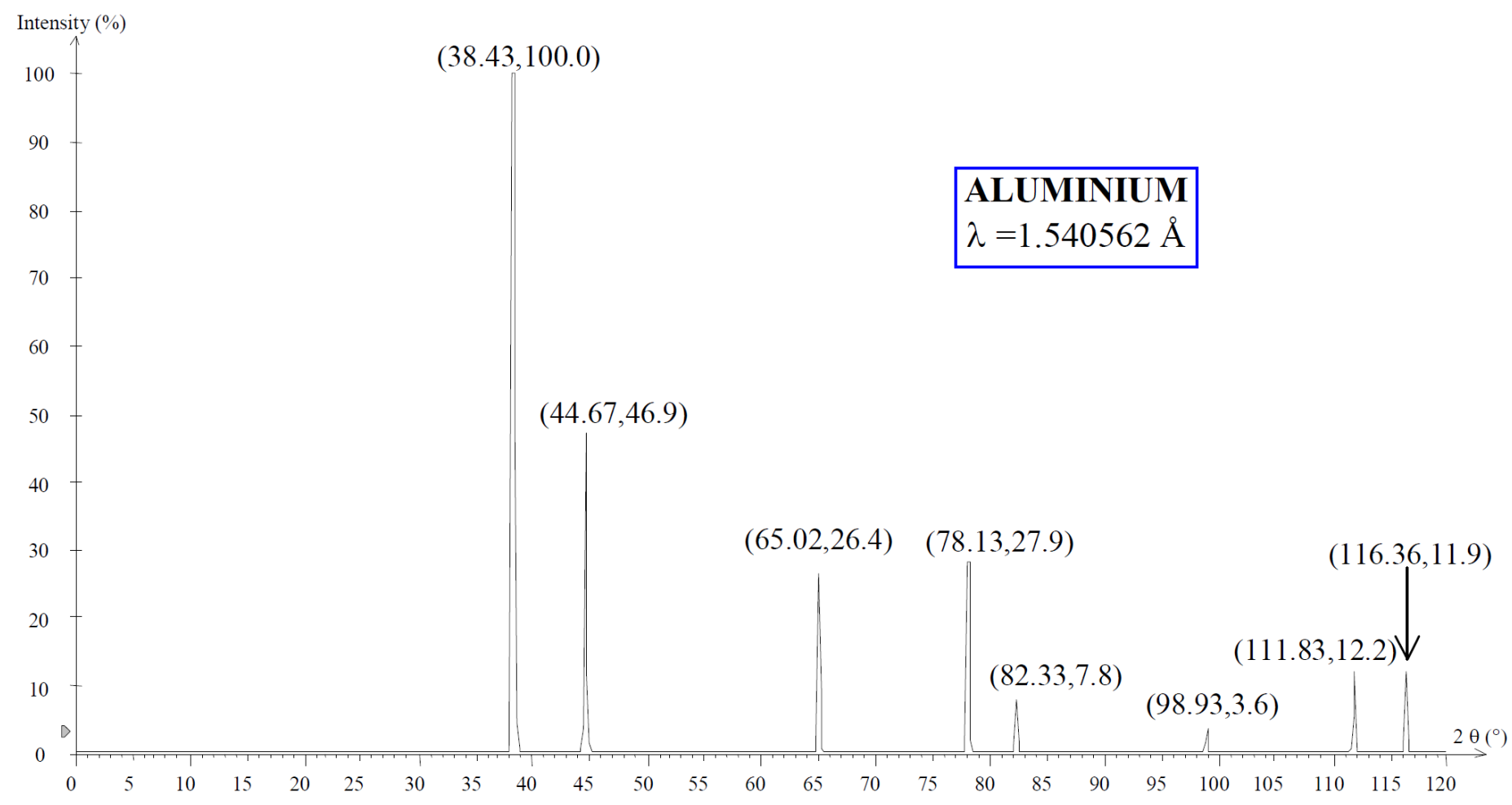
Body-centered  $h^2 + k^2 + l^2 = 2, 4, 6, 8, 10, 12, 14, 16 \dots$

Face-centered  $h^2 + k^2 + l^2 = 3, 4, 8, 11, 12, 16, 19, 20, 24, 27, 32 \dots$

Diamond cubic  $h^2 + k^2 + l^2 = 3, 8, 11, 16, 19, 24, 27, 32 \dots$

# Example

Consider the following XRD pattern for Aluminum, which was collected using  $\text{CuK}\alpha$  radiation.



Index this pattern and determine the lattice parameters.

# Example

- (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.
- (6) Calculate lattice parameters.

- (1) Identify the peaks and their proper  $2\theta$  values. Eight peaks for this pattern. Note: most patterns will contain  $\alpha_1$  and  $\alpha_2$  peaks at higher angles. It is common to neglect  $\alpha_2$  peaks.

Peak No.	$2\theta$	$\sin^2 \theta$	$1 \times \frac{\sin^2 \theta}{\sin^2 \theta_{\min}}$	$2 \times \frac{\sin^2 \theta}{\sin^2 \theta_{\min}}$	$3 \times \frac{\sin^2 \theta}{\sin^2 \theta_{\min}}$	$h^2+k^2+l^2$	$hkl$	$a$ (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							