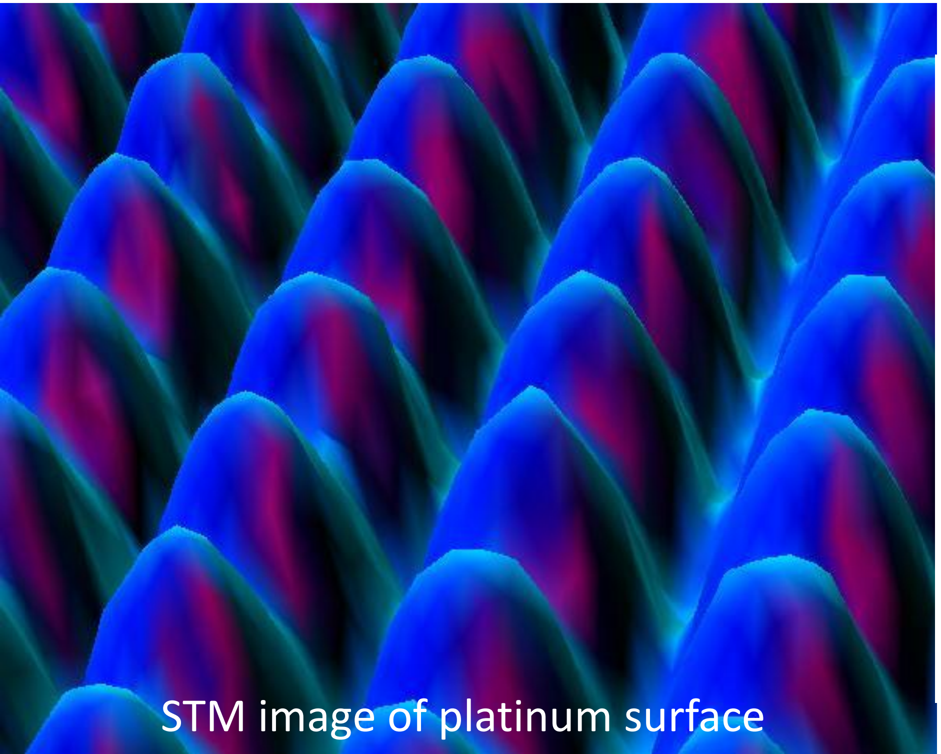
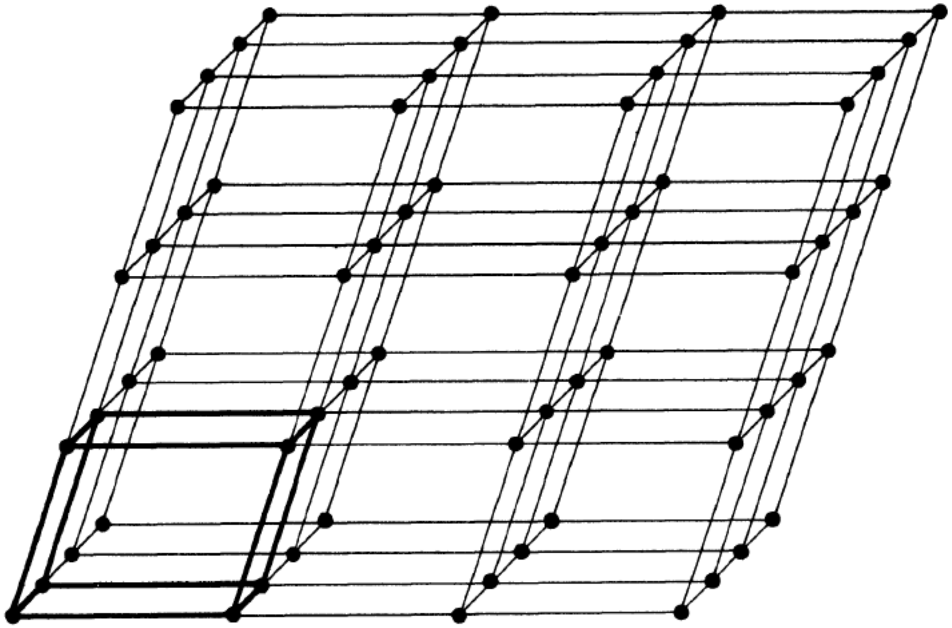
X-ray Techniques for Crystallinity Analysis

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

Molecular Crystal Structure Theory

The first comprehensive **molecular crystal structure theory** was the creation of the **Abbé René Just Haűy** (1743 – 1822).

Haűy, one of the few major scientists to be a catholic priest, had received a good scientific education and became interested in natural history (botany/mineralogy/crystallography).

In 1784, he published his ***Essai d'une théorie sur la structure des crystaux***, based on the unit of the compound **molécule intégrante**, **specific in shape and composition for every compound.**

ESSAI
D'UNE THÉORIE
SUR LA STRUCTURE
DES CRYSTAUX,
APPLIQUÉE

A PARIS,

Haűy'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**.

Haűy's Theory: Crystal Structure

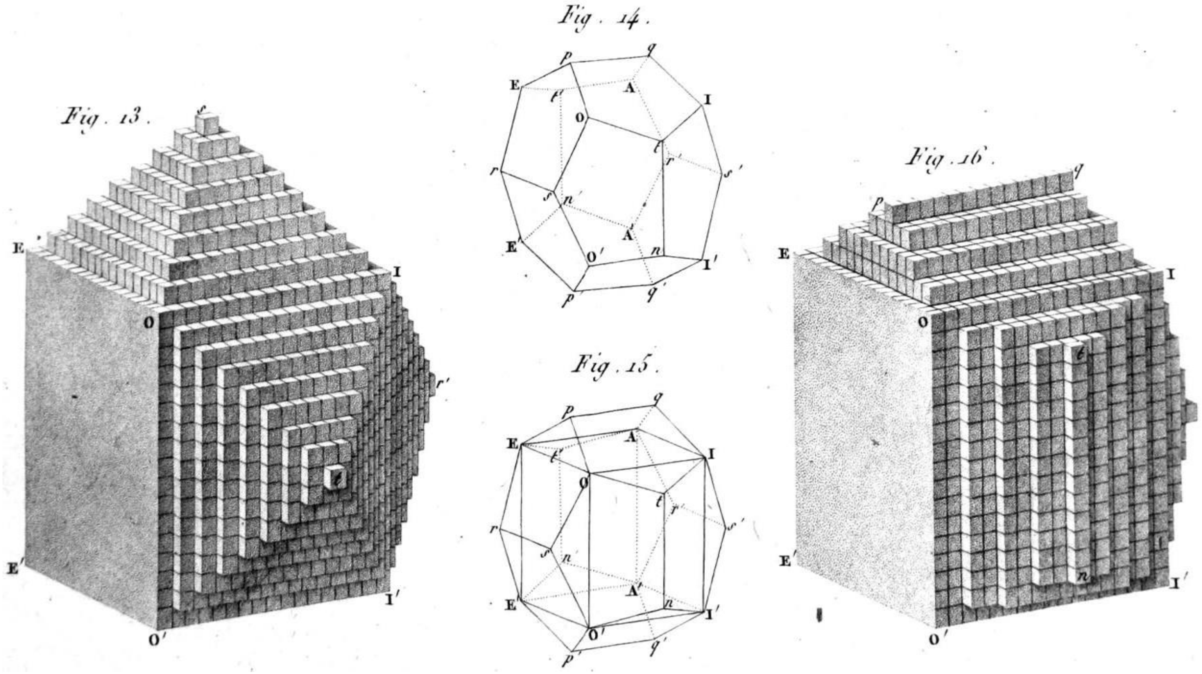
Haűy's molecular structural models

Traité de Minérologie

(1801). Fig. 13 & 16:

cubic *molécules intégrantes,*

cubic *primitive form*



simple decrement

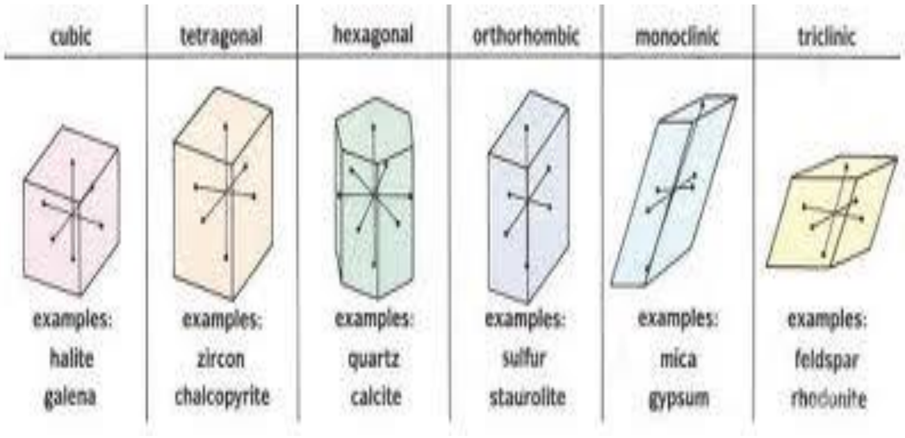
rhomb-dodecahedron (Fig. 13)

complex decrements

pentagon-dodecahedron (Fig. 16)

Crystalline Symmetry & Systems

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



This was initiated early in the 19th 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 19th 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

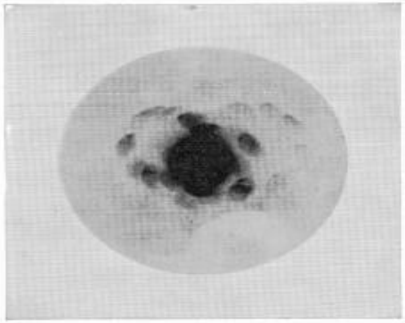


Fig. 4-4(1). Friedrich & Knipping's first successful diffraction photograph.

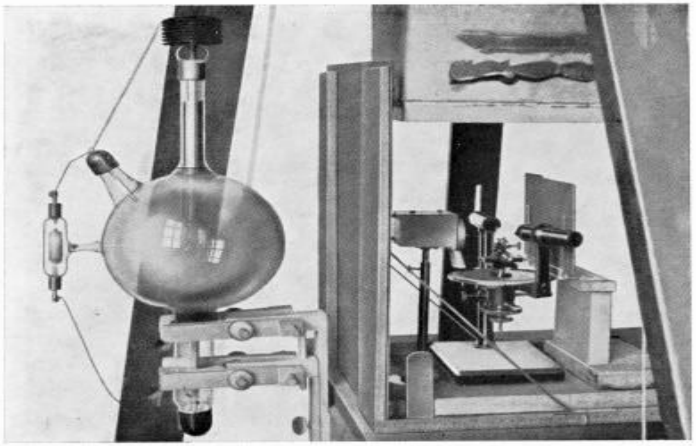


Fig. 4-4(2). Friedrich & Knipping's improved set-up.

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).

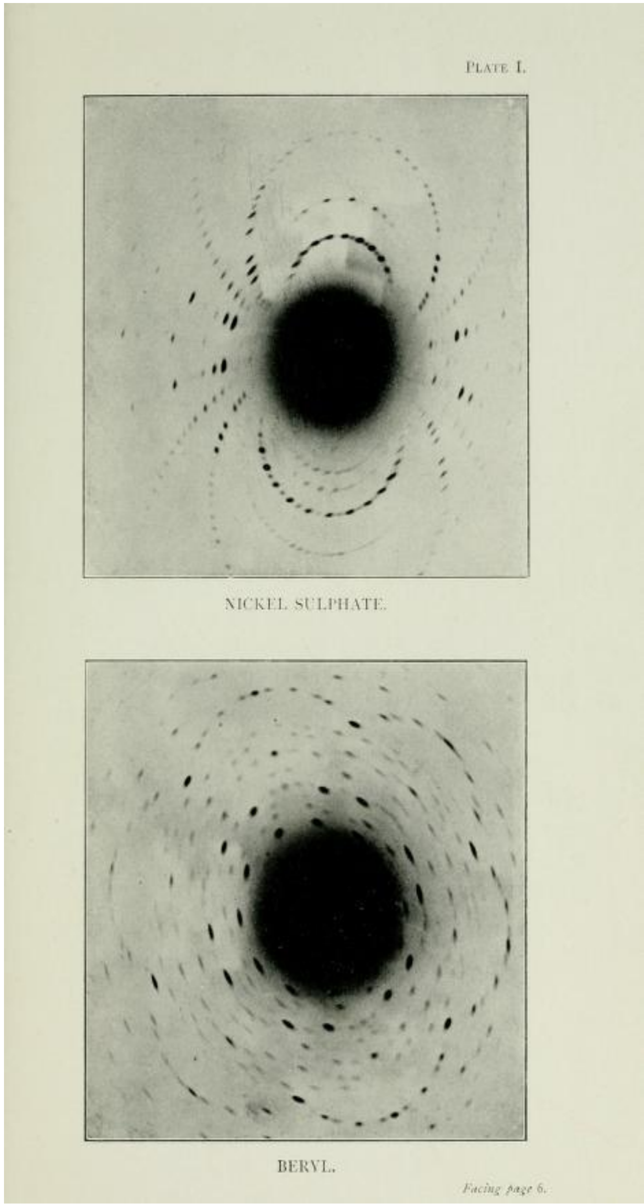


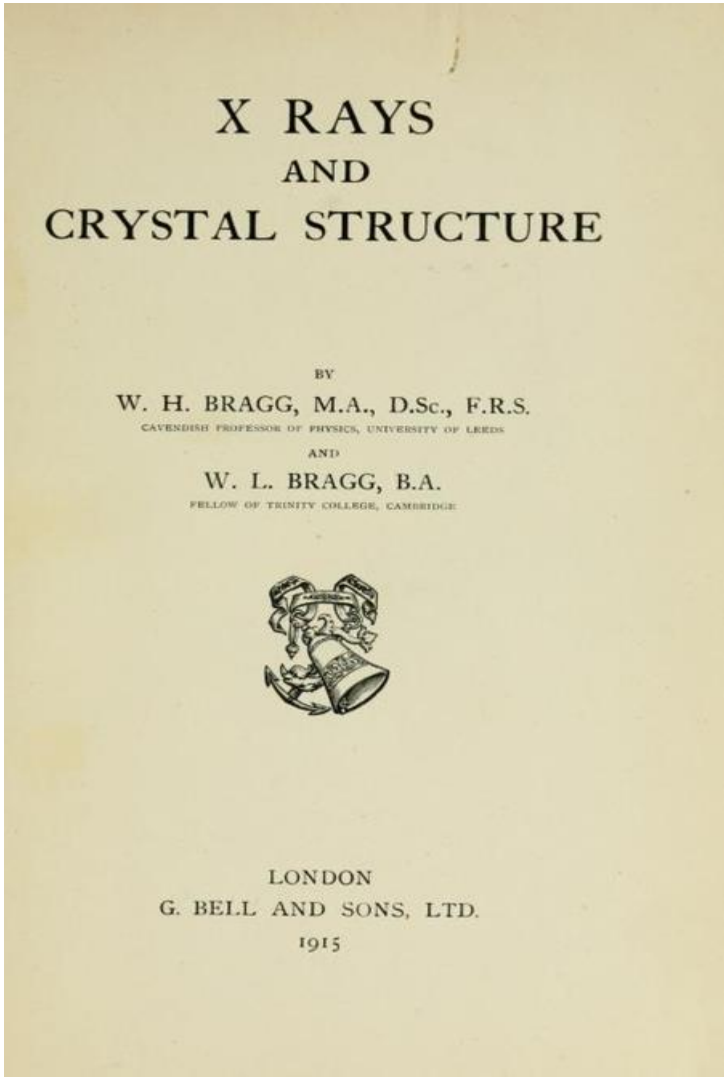
PLATE I.

NICKEL SULPHATE.

BERYL.

Facing page 6.

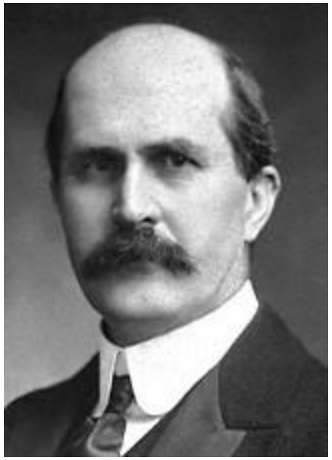
W. H. & W. L. Bragg, *X-Rays and Crystal Structure* (1915)

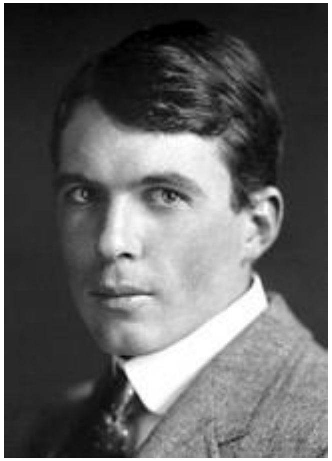


X RAYS
AND
CRYSTAL STRUCTURE

BY
W. H. BRAGG, M.A., D.Sc., F.R.S.
CAVENDISH PROFESSOR OF PHYSICS, UNIVERSITY OF LEEDS
AND
W. L. BRAGG, B.A.
FELLOW OF TRINITY COLLEGE, CAMBRIDGE

LONDON
G. BELL AND SONS, LTD.
1915





Photos

Top: William Henry Bragg (1862 – 1942);

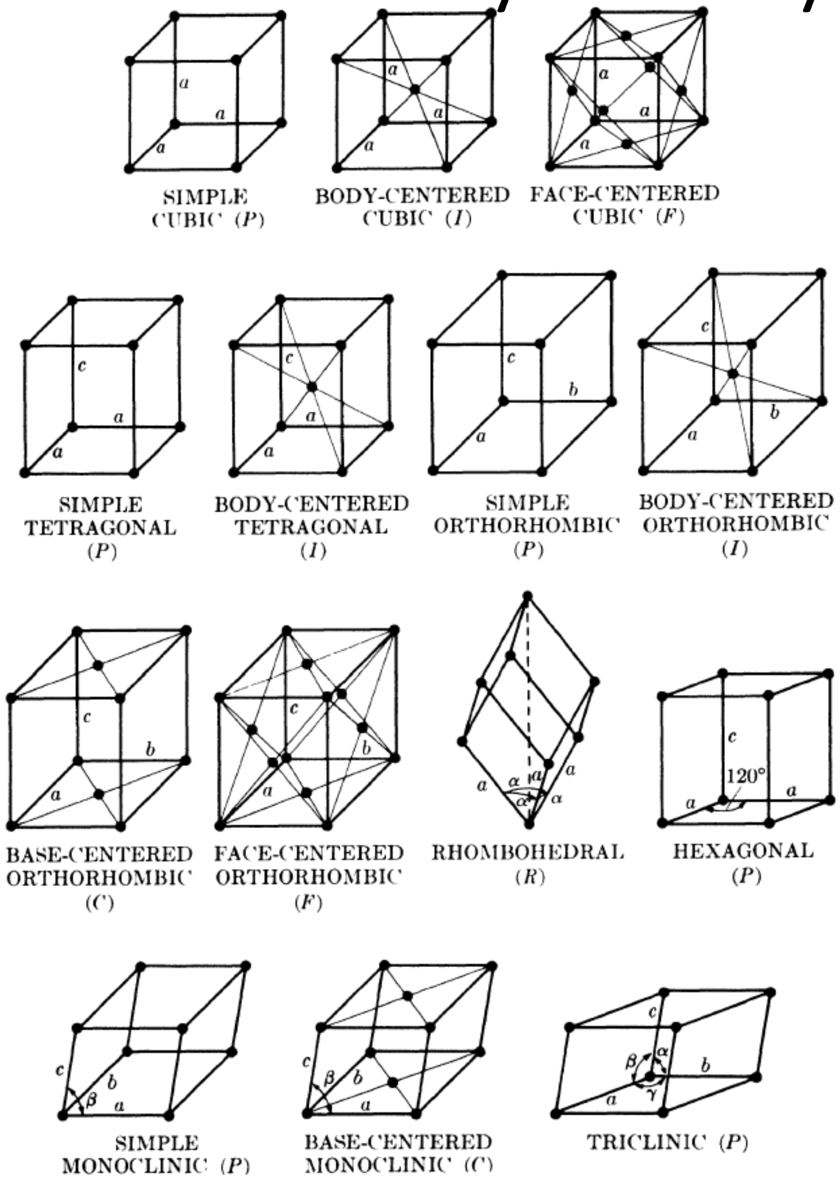
Bottom Wlliam Lawrence Bragg

(1890-1971)

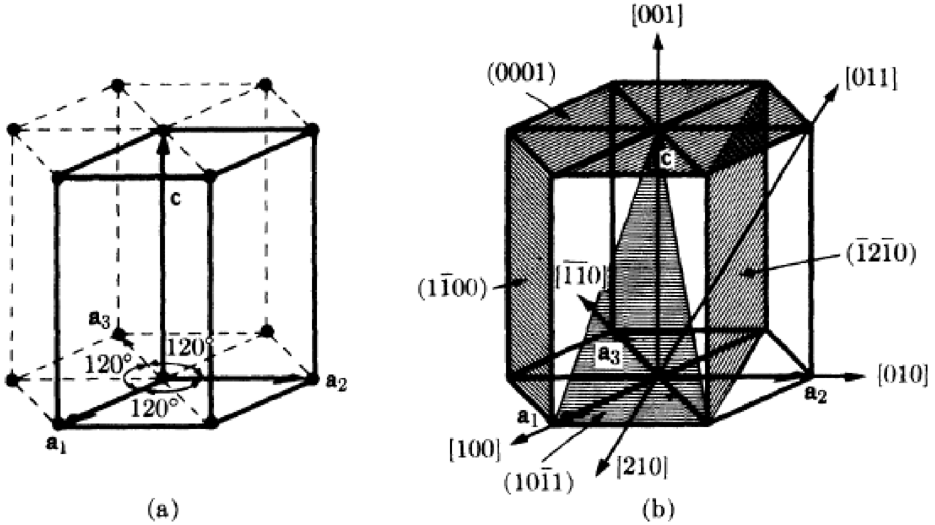
Swedish postage stamp with Braggs

Geometry of Crystals

- 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.



14 point lattices found in nature



(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.

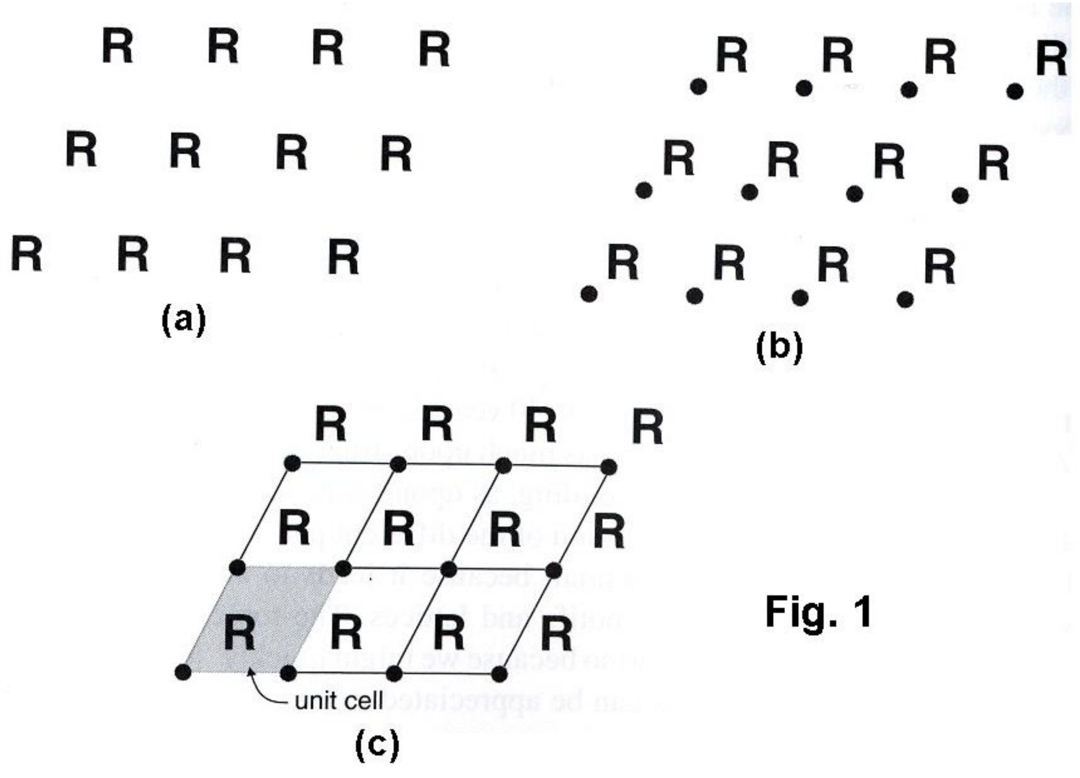


Fig. 1

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.

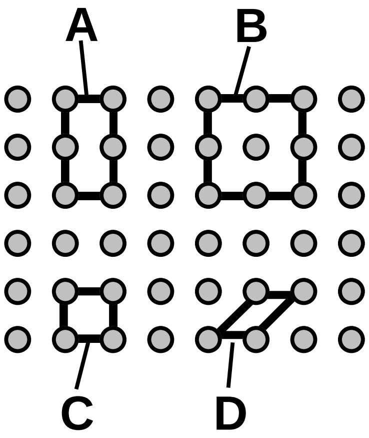


Fig. 2

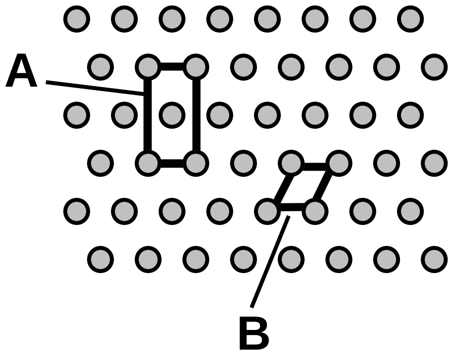
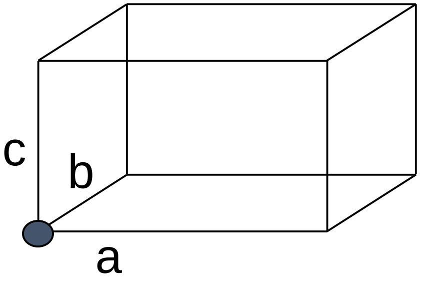


Fig. 3

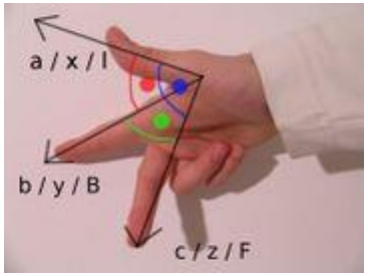
There is no unique way of choosing a unit cell. For example, each of the cells (**A** to **D**) in Fig. 2 are OK. However, the cell favoured by crystallographers is the one of smallest volume that displays all of the symmetry of the lattice. Thus, cells **C** and **A** are the preferred unit cells for 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 α, β, and γ). In the strict mathematical sense, a, b, and c are vectors since they specify both length and direction. α is the angle between b and c, β is the angle between a and c, γ 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.

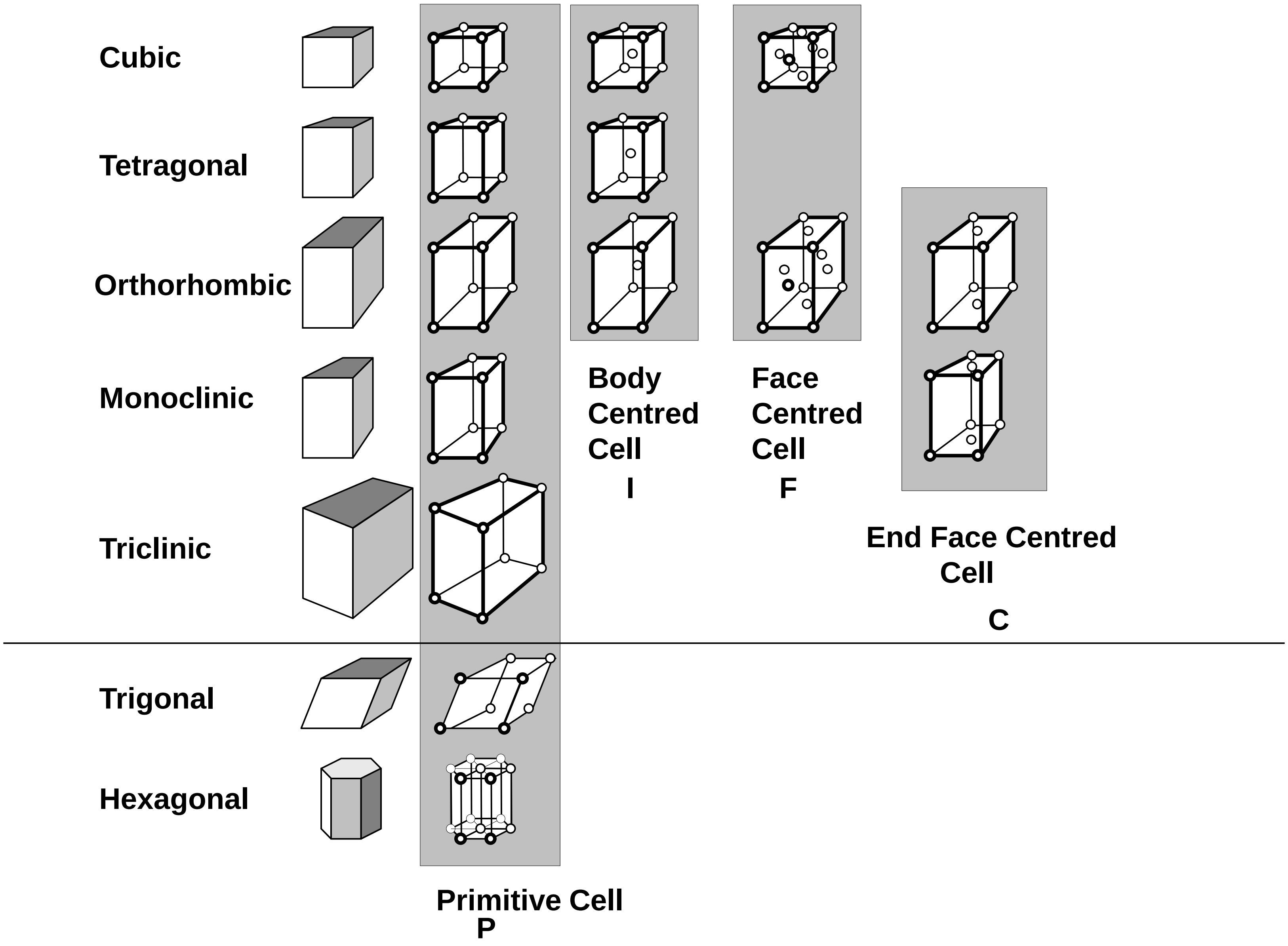

Cubic
Tetragonal
Orthorhombic
Monoclinic
Triclinic
Trigonal
Hexagonal
Body Centred Cell
I
Face Centred Cell
F
End Face Centred Cell
C
Primitive Cell
P

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.

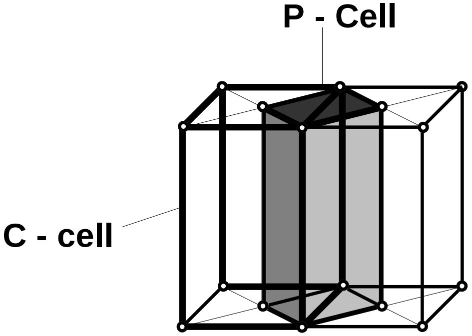


Fig. 4

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

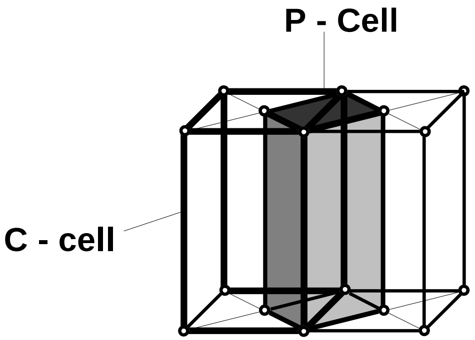
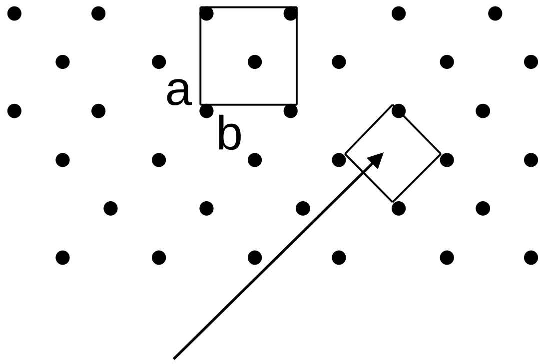


Fig. 4

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

Tetragonal

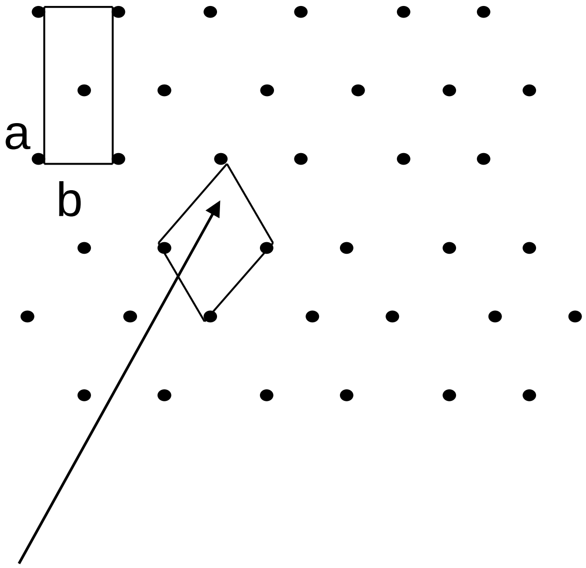
$a = b \neq c, a = b = \gamma = 90^{o}$



Smaller cell is Tetragonal P

Orthorhombic

$a \neq b \neq c, a = b = \gamma = 90^{o}$



Angle not 90° 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	**Symmetry Operation**
Rotation axis (n-fold)	Rotation
Mirror plane	Reflection
Centre of Symmetry	Inversion
Rotor-reflection axis (n-fold)	Rotation and reflection
or	
Rotor-inversion axis (n-fold)	Rotation and inversion

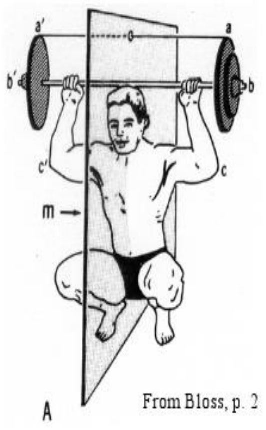
Symmetry Elements and Operations

“***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.

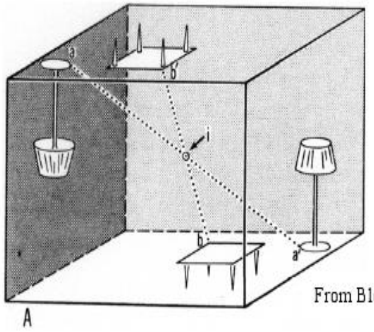
Symmetry Operations ---} 32 Point Groups

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



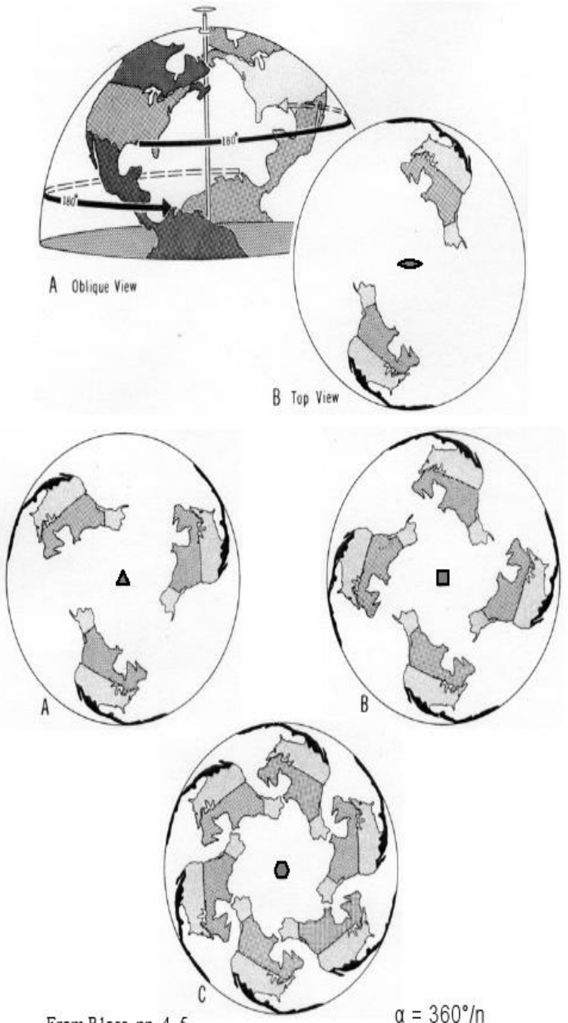
From Bloss, p. 2

2. REFLECTION = *m*



From Bloss, p. 6

4. INVERSION = *i*



From Bloss, pp. 4, 5

α = 360°/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.

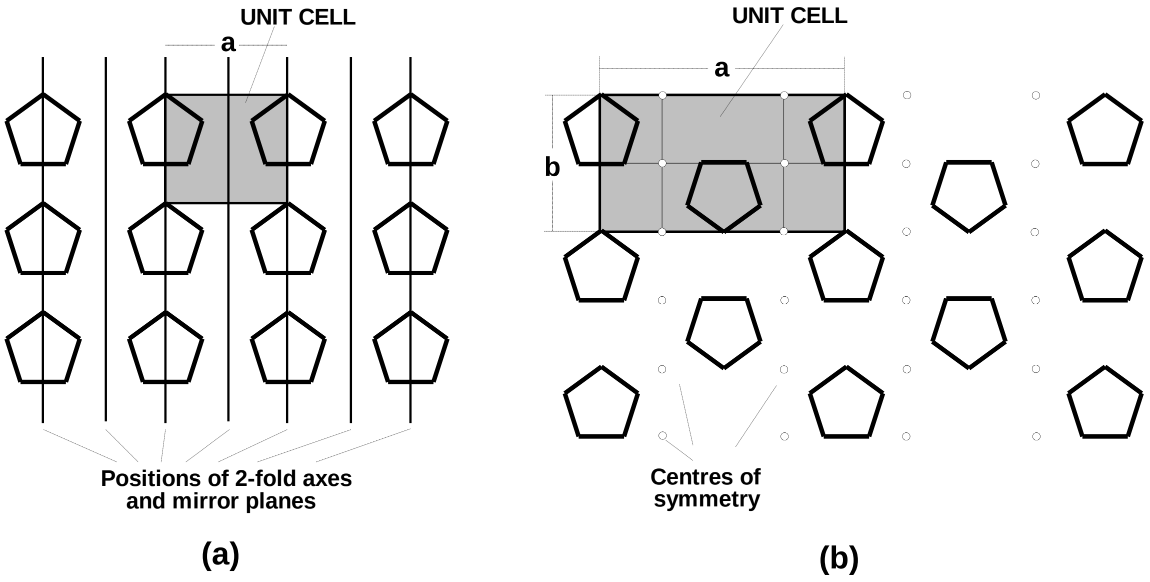
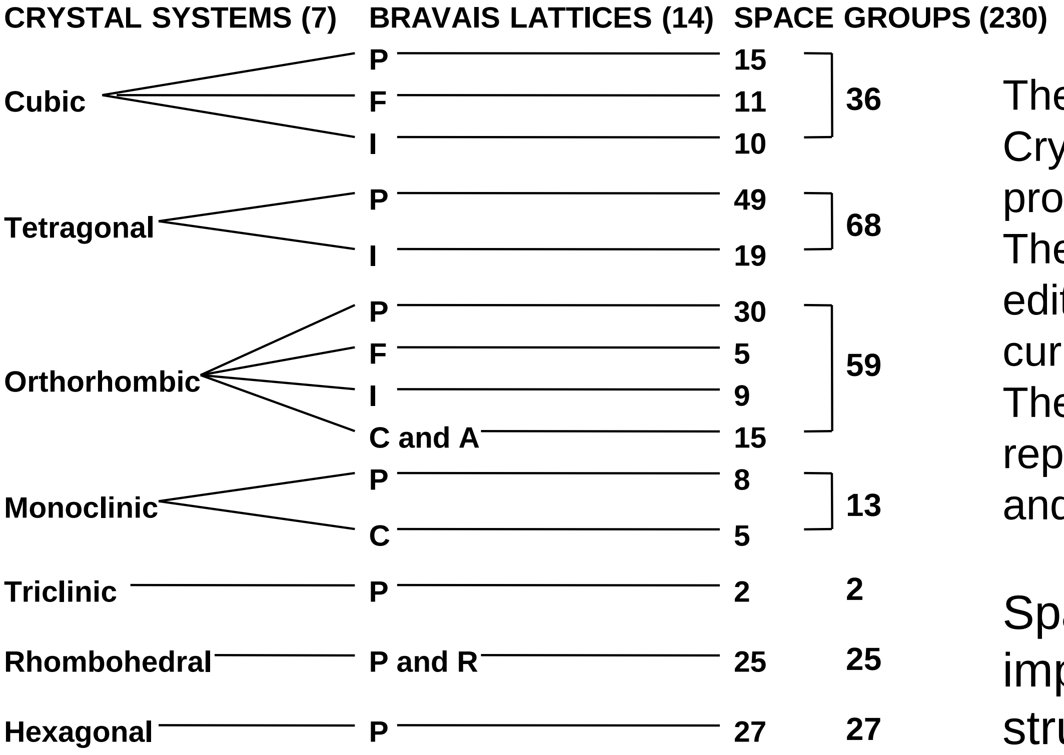


Fig. 5

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	36
	F	11	
	I	10	
Tetragonal	P	49	68
	I	19	
Orthorhombic	P	30	59
	F	5	
	I	9	
	C and A	15	
Monoclinic	P	8	13
	C	5	
Triclinic	P	2	2
Rhombohedral	P and R	25	25
Hexagonal	P	27	27

Fig. 9

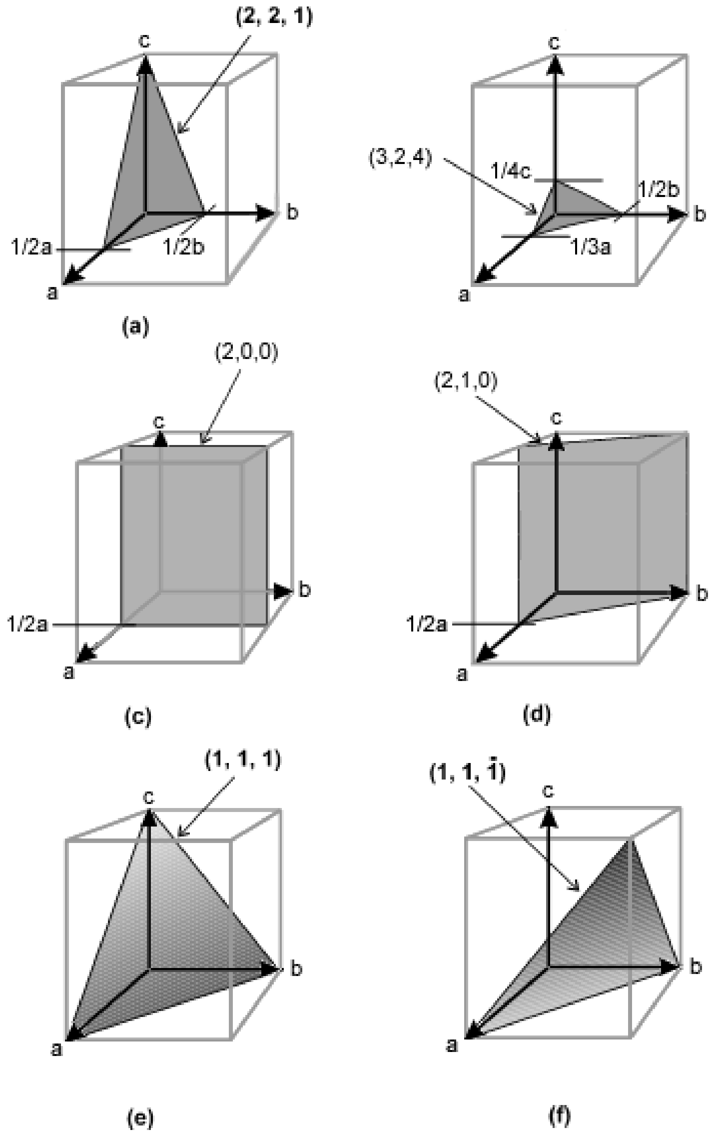
The International Tables for Crystallography list the symmetry properties for all 230 Space Groups. The 2nd edition was in one volume and edited by Kathleen Lonsdale. The current edition runs to 7 volumes. The CSD or Cambridge Data Base is a repository for the structures of organic and organometallic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

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

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 ½, ½, 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 -1). In crystallography -1 is often written ī 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 a mirrors. Constructive interference is observed when the path difference between the two reflected beams in (a) = nλ. The path difference in (a) is 2my. Since my/d = sinθ

2my = 2dsin$\theta = $ nλ

where d is the interplanar spacing.

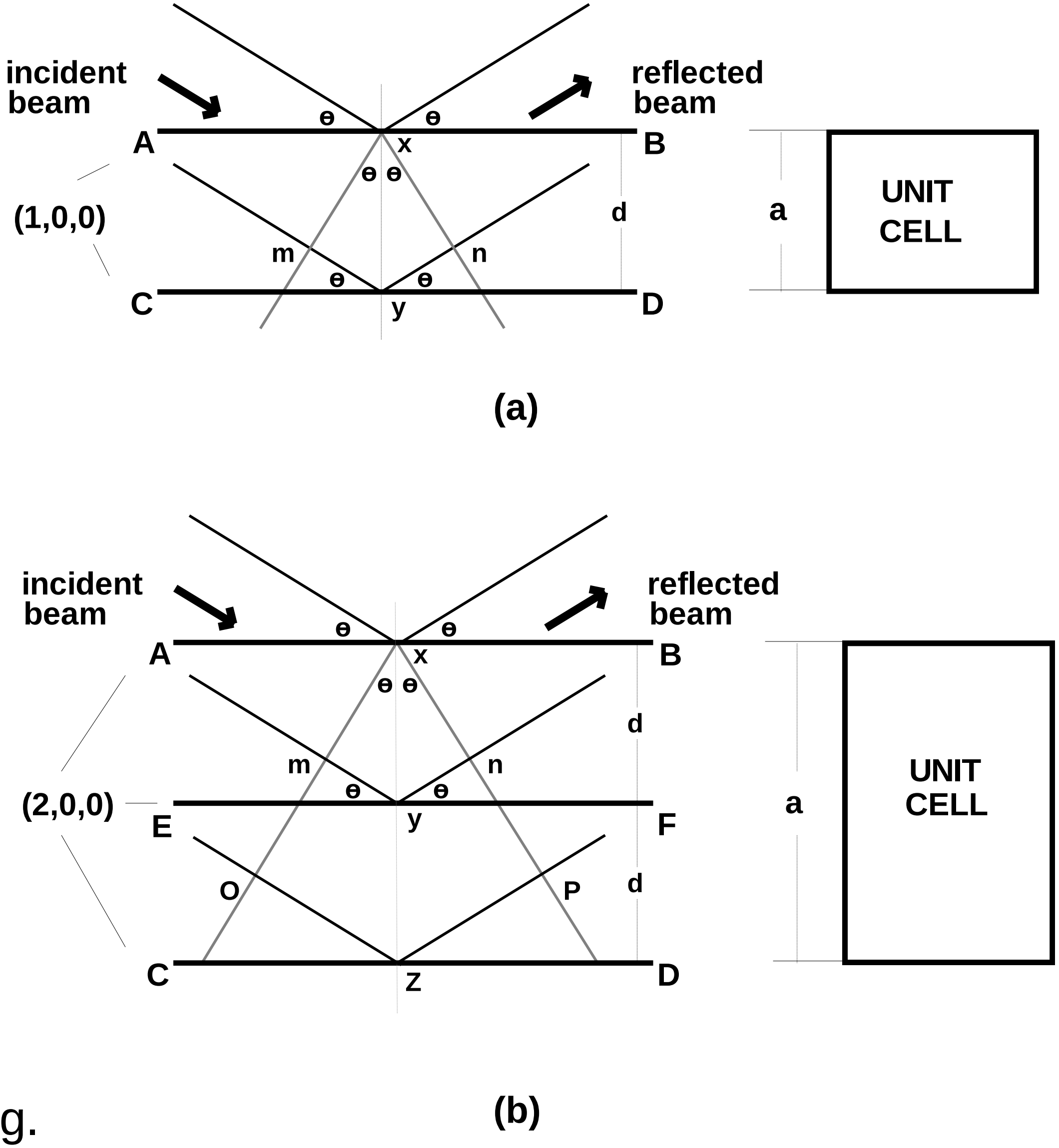


Fig. 11

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

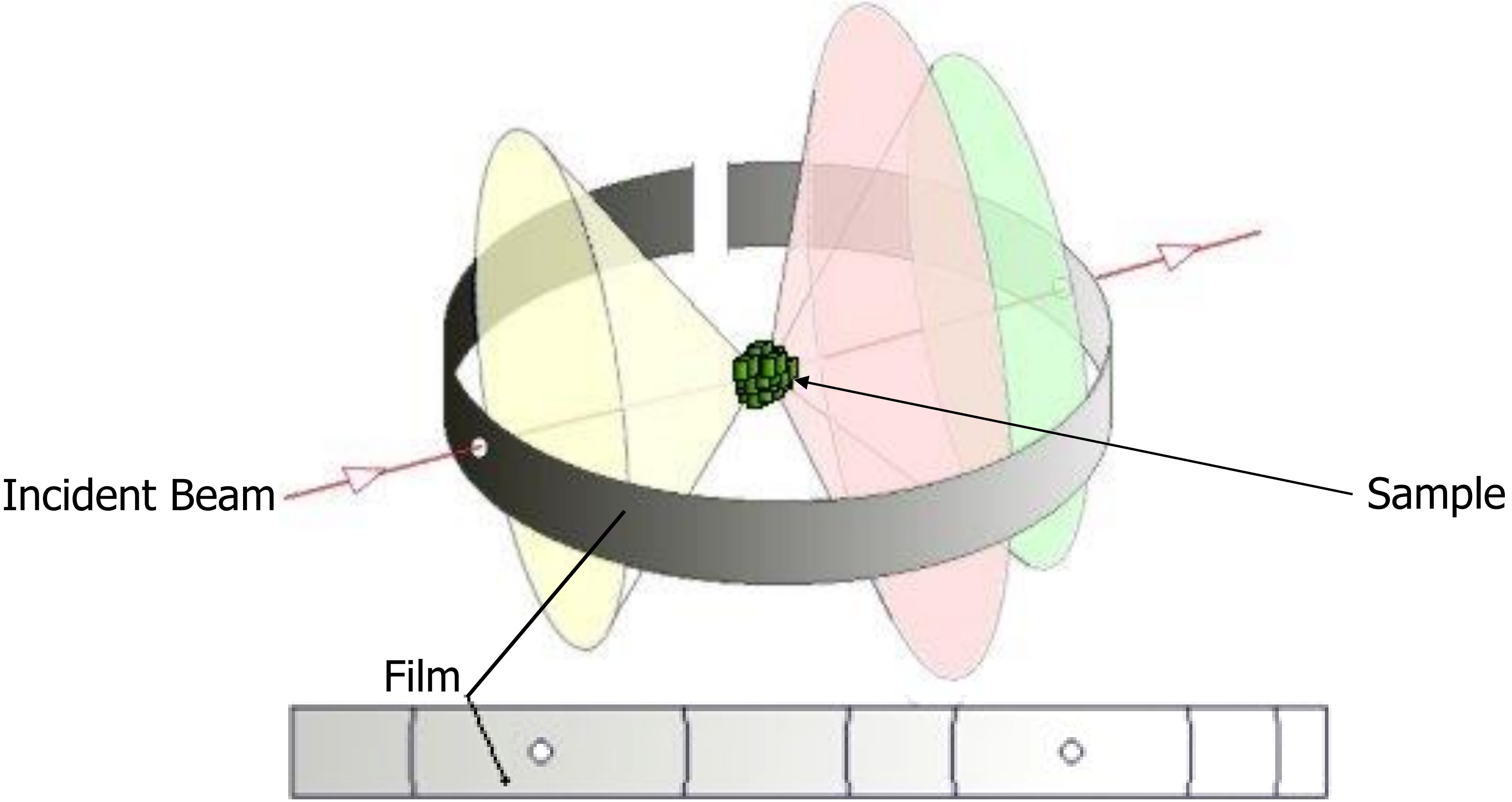
$$2d_{(1,0,0)} \sin\theta = \lambda$$

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***.

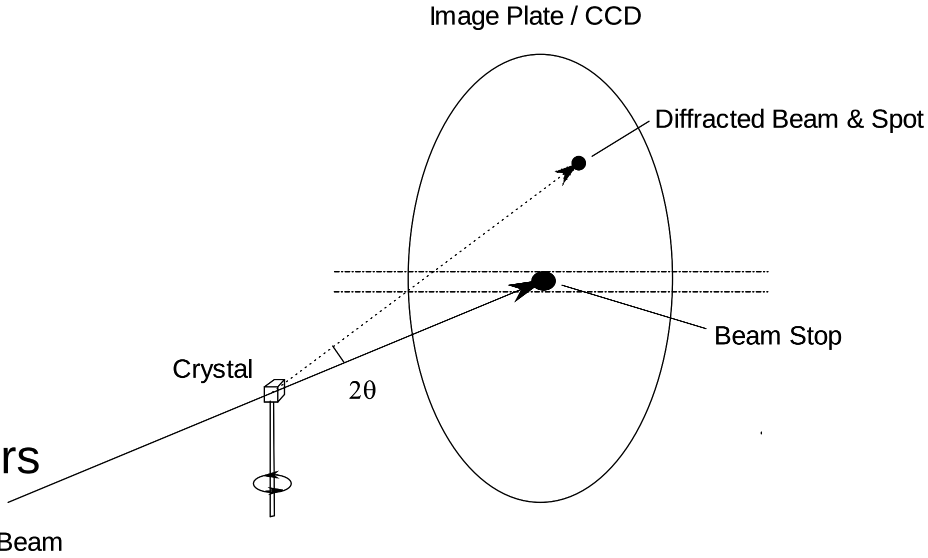
Powder Method

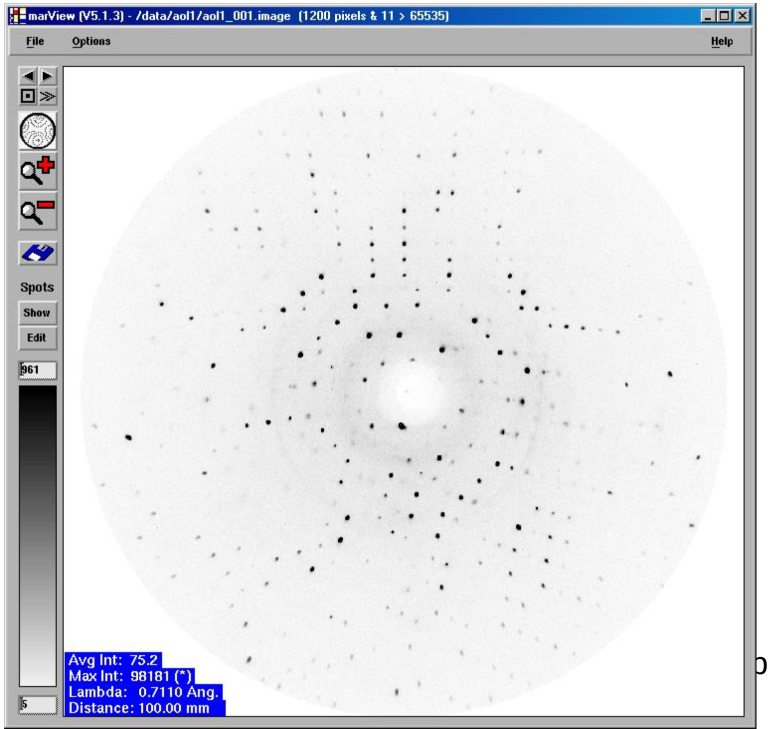


- Useful for determining lattice parameters with high precision and for identification of phases

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.




marView (V5.1.3) - /data/aol1/aol1_001.image (1200 pixels & 11 > 65535)

Avg Int: 75.2
Max Int: 98181 (*)
Lambda: 0.7110 Ang.
Distance: 100.00 mm

The crystal is oscillated over < 2° 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°. Each image is exposed for < 100s. Thus if readout time is ignored total data collection time is often < 3 hr.

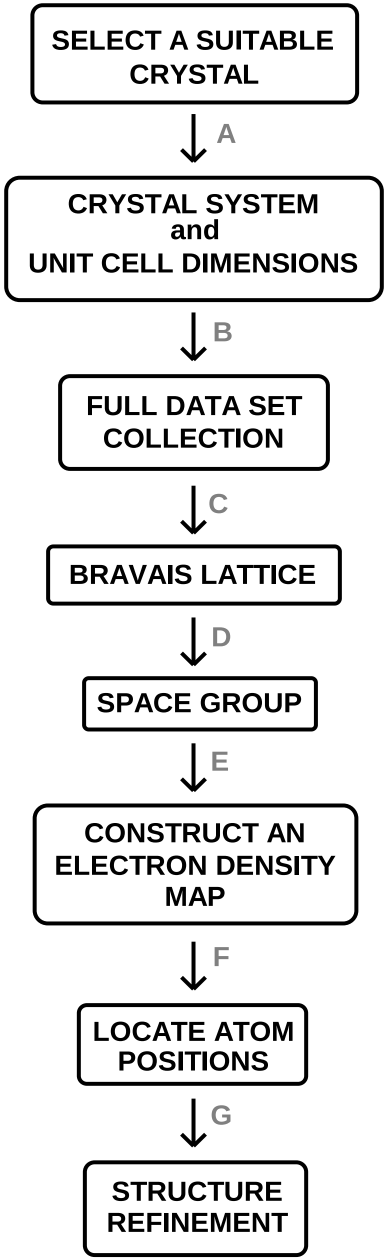
A typical image shown to the left.

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.



SELECT A SUITABLE CRYSTAL

A

CRYSTAL SYSTEM and UNIT CELL DIMENSIONS

B

FULL DATA SET COLLECTION

C

BRAVAIS LATTICE

D

SPACE GROUP

E

CONSTRUCT AN ELECTRON DENSITY MAP

F

LOCATE ATOM POSITIONS

G

STRUCTURE REFINEMENT

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 α $|F|^2$

- 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) ………
BCC	(110), (200), (211), (220), (310), (222)….
FCC	(111), (200), (220), (311)…..

Calculations using X-ray powder diffraction patterns

For an orthogonal system ($\alpha = \beta = \gamma = 90°$) 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

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

Cubic unit cell

Bragg's law becomes

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

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

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

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

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

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

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

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, …

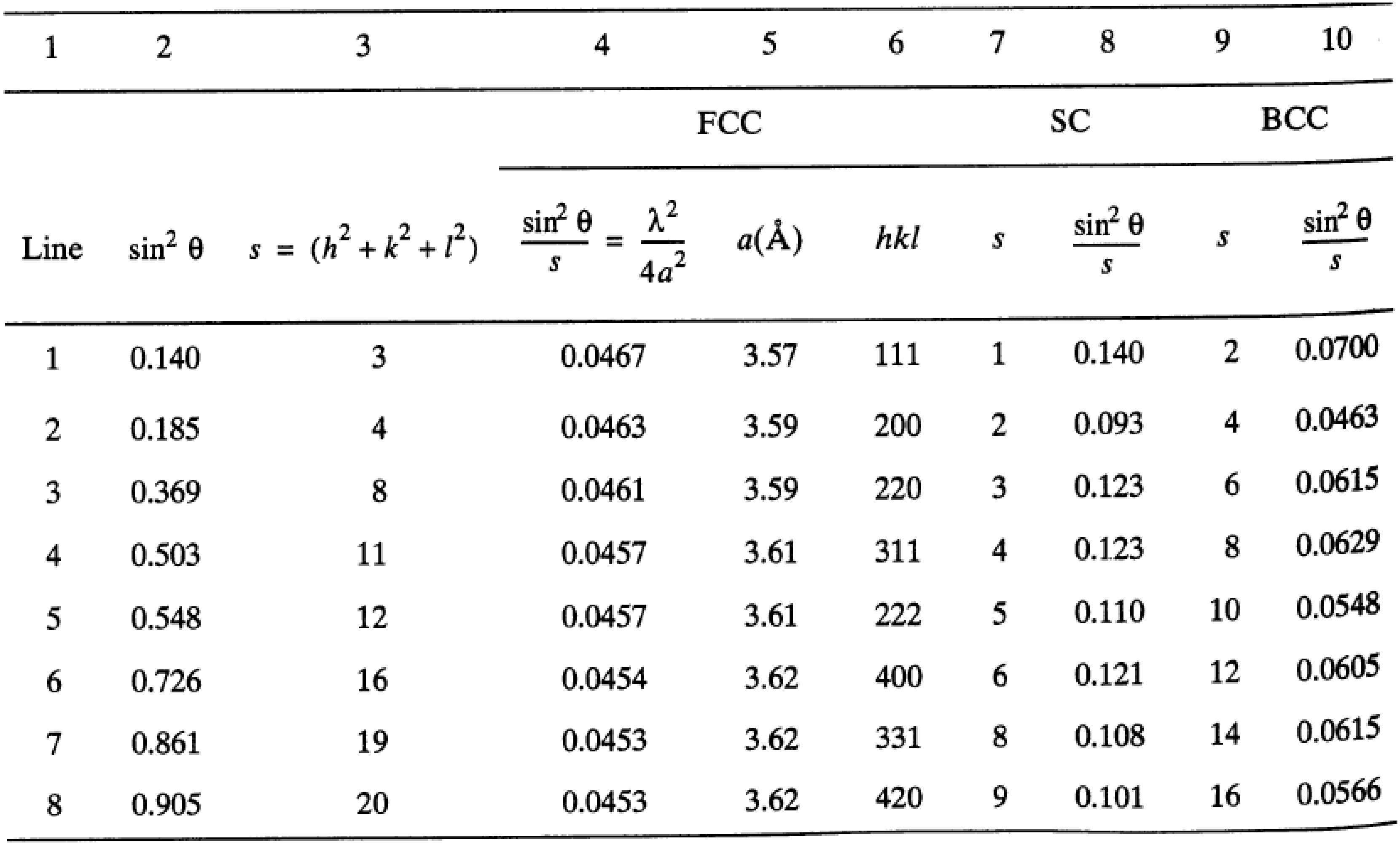
Face-centered cubic: 3, 4, 8, 11, 12, 16, 19, 20, 24, 27, 32, …

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



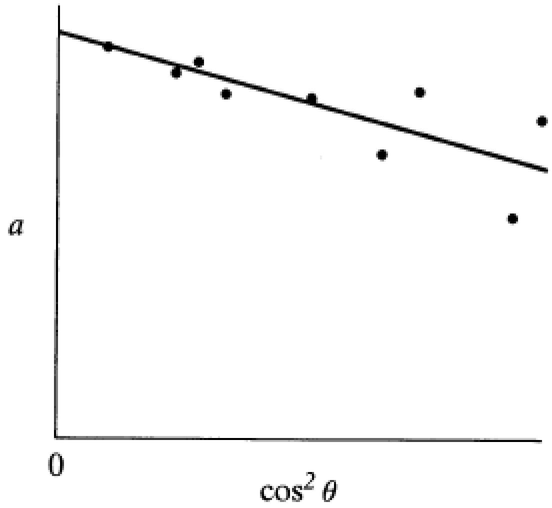
1	2	3	4	5	6	7	8	9	10
			FCC			SC		BCC	
Line	$\sin^2\theta$	$s = (h^2 + k^2 + l^2)$	$\frac{\sin^2\theta}{s} = \frac{\lambda^2}{4a^2}$	a(Å)	hkl	s	$\frac{\sin^2\theta}{s}$	s	$\frac{\sin^2\theta}{s}$
1	0.140	3	0.0467	3.57	111	1	0.140	2	0.0700
2	0.185	4	0.0463	3.59	200	2	0.093	4	0.0463
3	0.369	8	0.0461	3.59	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

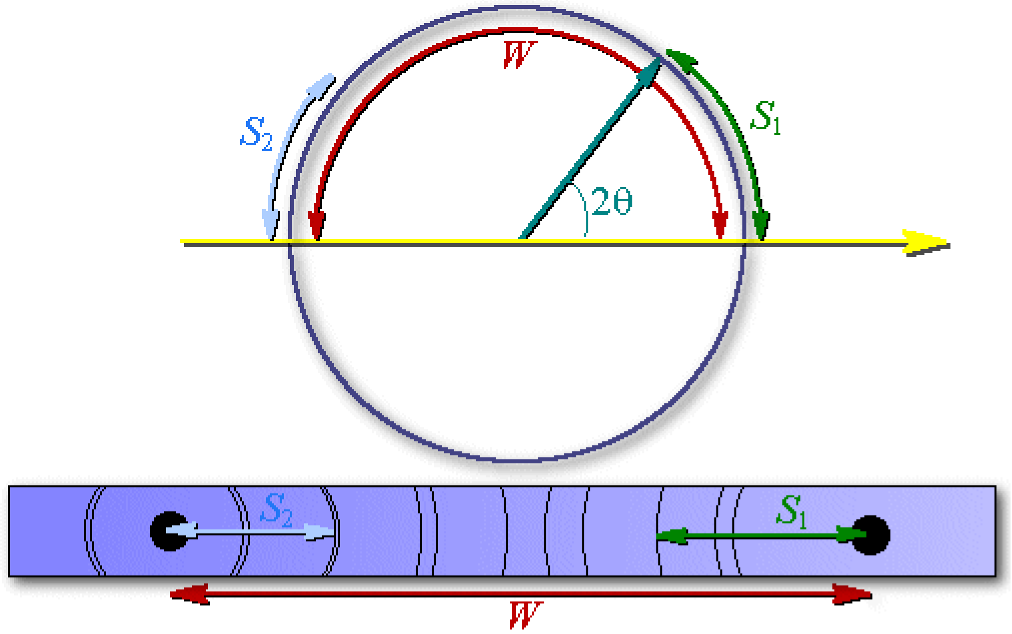
- Calculation of the lattice parameter from one peak is prone to error due to
  - Displacement of the specimen from the diffractometer axis
  - Misalignment of the instrument
  - Use of a flat specimen instead of a speciment curved to confrom to the focusing circle
  - Absorption in the specimen
  -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

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

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



Indexing a Laue powder pattern



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

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

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

For cubic crystals

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

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

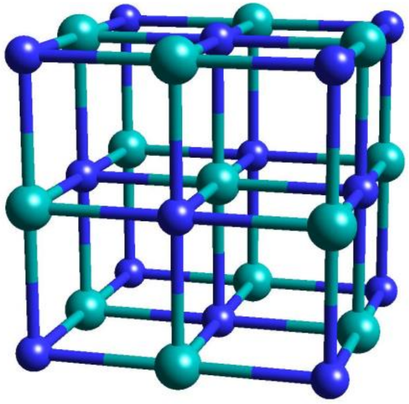
Indexing

FCC; wavelength=1.54056Å					
S_1 (mm)	θ(°)	$\sin^2\theta$	$h^2+k^2+l^2$	$\sin^2\theta/ h^2+k^2+l^2$	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
				Constant; so it is FCC	

Important Cubic Lattice Types

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

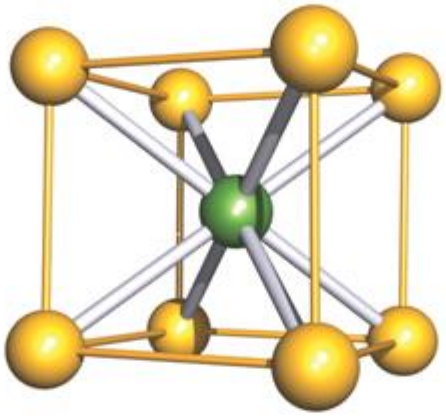
NaCl crystallizes in the Space Group **Fm-3m**



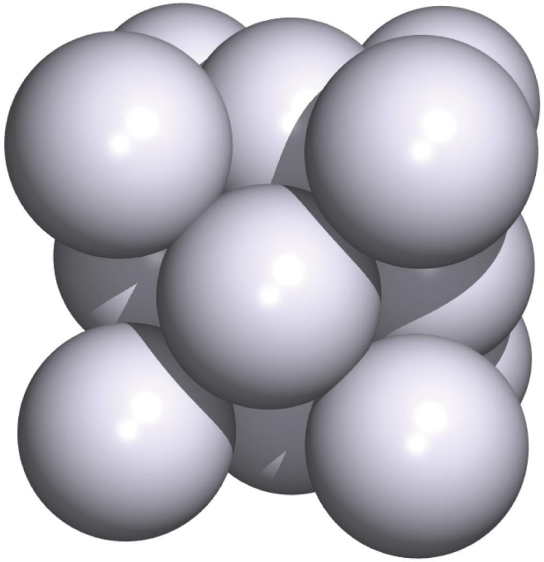
Stoichiometry (formula) from the Unit Cell

Site	Na^+	Cl^-
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 x 1/8Cl = 1 = 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:
$6 \times \frac{1}{2} + 8 \times 1/8 = 4$

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^3):	8.90
Volume of cell (10^6 pm^3):	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 λ = 1.5405 A .
Index the diffraction data and calculate the density of aluminium.

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

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 $\boxed{\sin^2\theta = A(h^2 + k^2 + l^2)}$ 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 sinθ 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	Sinθ	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

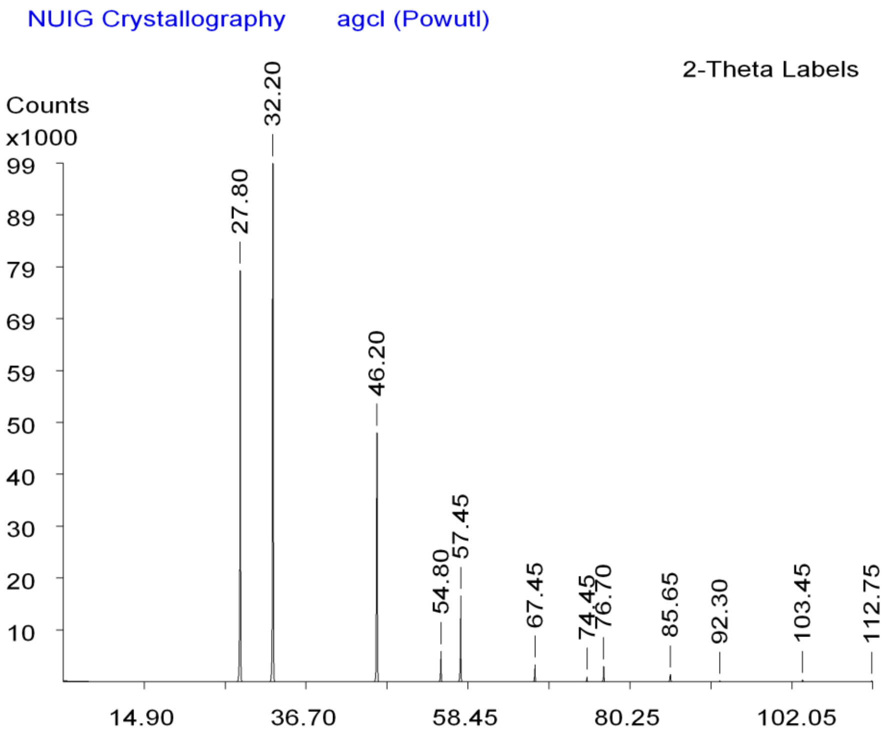
For the first reflection (for which $h^2 + k^2 + l^2 = 3$)
$\sin^2\theta = 3A = 3 (\lambda^2 / 4a^2)$
$a^2 = 3\lambda^2 / 4\sin^2\theta$
a = 4.04946 Å = 4.04946 x 10^{-8} cm.

Calculation of the density of aluminium

a^3 = 66.40356 $Å^3$ = 66.40356 x 10^{-24} cm^3.
If the density of aluminium is ρ (g. $cm.^{-3}$), the mass of the unit cell is
ρ x 66.40356 x 10^{-24} g.

The unit cell of aluminium contains 4 atoms.
The weight of one aluminium atom is 26.98/(6.022 x 10^{23}) = 4.48024 x 10^{-23}
and the weight of four atoms (the content of the unit cell) is 179.209 x 10^{-24}.
ρ x 66.40356 x 10^{-24} = 179.209 x 10^{-24}
p = 2.6988 g.cm^{-3}.

Example-2 The X-ray powder diffraction pattern of AgCl obtained using radiation of wavelength 1.54Å is shown below. The peaks are labelled with 2θ 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 x 1023)

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

2θ	θ	Sin$^2\theta$
27.80	13.90	0.0577
32.20	16.10	0.0769
46.20	23.10	0.1539
54.80	27.40	0.2118
57.45	28.73	0.2310
67.45	33.73	0.3083

Calc. Sin$^2\theta$
0.07693
0.1539
0.2116
0.2308
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.*

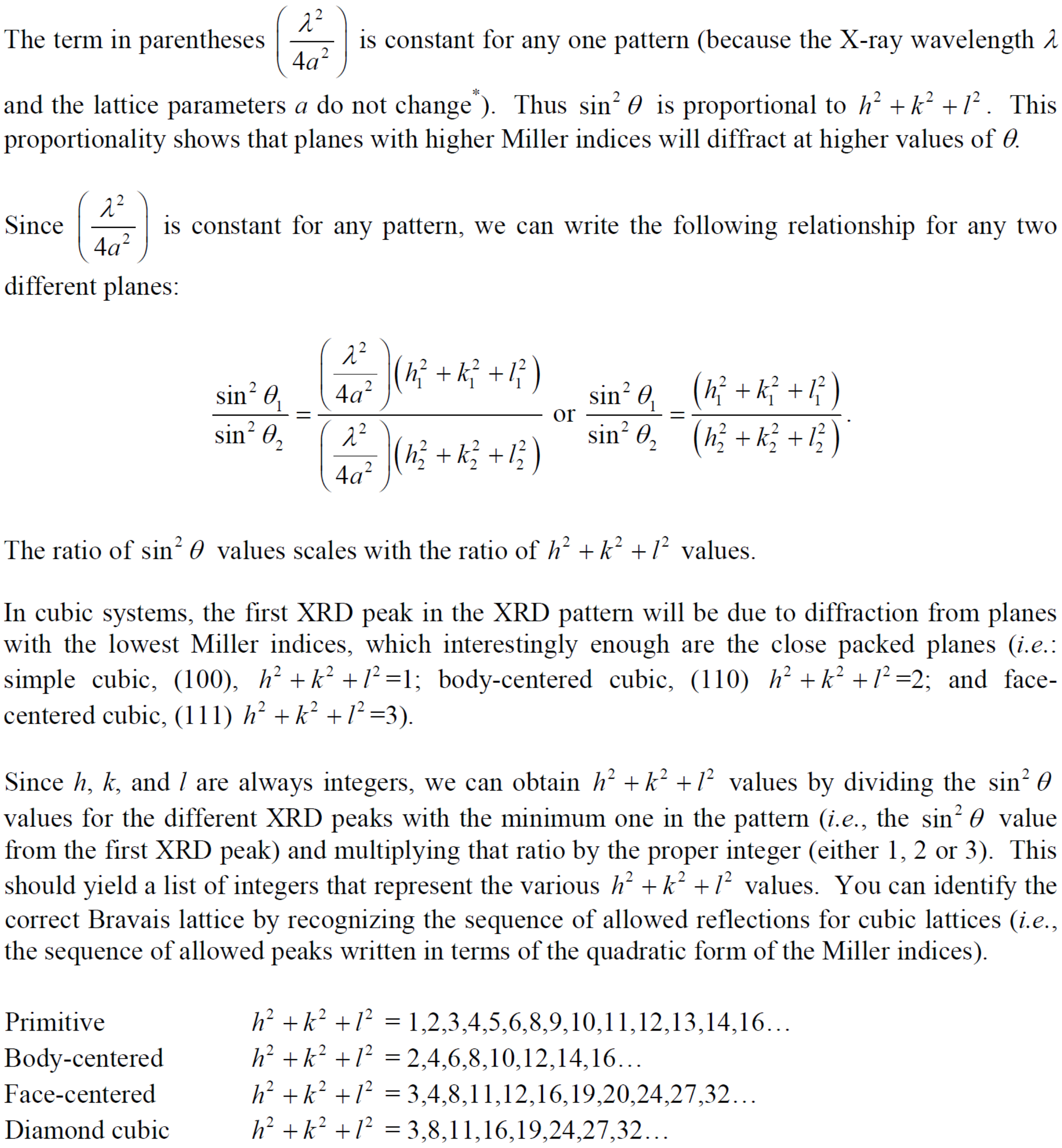
Density of AgCl

Since $\sin^2\theta = \lambda^2(h^2 + k^2 + l^2)/4a^2$
$a^2 = (1.54)^2.(16)/4(0.3083)$ using the largest (most accurate) 2θ
$a^2 = 30.7692$
$a = 5.547$Ǻ (1Ǻ = 10^{-8} cm)
Formula wt. of unit cell = 4AgCl = 573.284g
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 Ǻ thus the answer should be multiplied by $1 / 10^{-24}$

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

General procedure

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



The term in parentheses $\left(\frac{\lambda^2}{4a^2}\right)$ is constant for any one pattern (because the X-ray wavelength λ 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 θ.

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

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

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

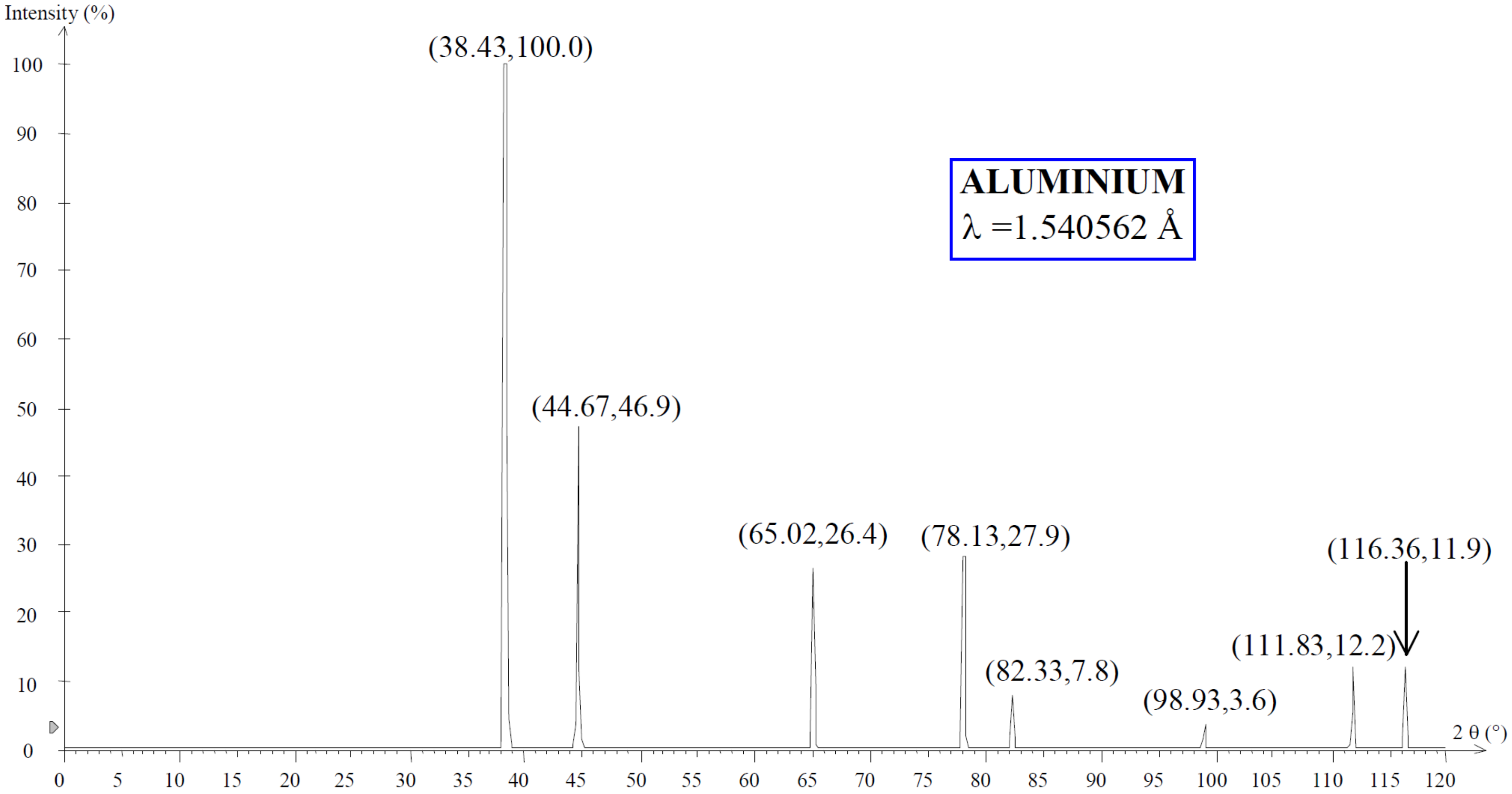
In cubic systems, the first XRD peak in the XRD pattern will be due to diffraction from planes with the lowest Miller indices, which interestingly enough are the close packed planes (*i.e.*: simple cubic, (100), $h^2+k^2+l^2=1$; body-centered cubic, (110) $h^2+k^2+l^2=2$; and face-centered cubic, (111)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

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

Example

Consider the following XRD pattern for Aluminum, which was collected using CuKα 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 2θ values. Eight peaks for this pattern. Note: most patterns will contain α_1 and α_2 peaks at higher angles. It is common to neglect α_2 peaks.

Peak No.	2θ	$\sin^2\theta$	$1\times\dfrac{\sin^2\theta}{\sin^2\theta_{\min}}$	$2\times\dfrac{\sin^2\theta}{\sin^2\theta_{\min}}$	$3\times\dfrac{\sin^2\theta}{\sin^2\theta_{\min}}$	$h^2+k^2+l^2$	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							

X-RAY FLUORESCENCE (XRF)

X-ray florescence spectroscopy enables determining elemental composition of samples by analyzing the characteristic X-rays that are emitted from the samples. High energy primary X-rays are used to generate these secondary X-rays.

Characteristic X-rays can be analyzed based on their wavelengths or energies.

There are two types of XRF methods:

Wavelength dispersive spectroscopy (WDS)

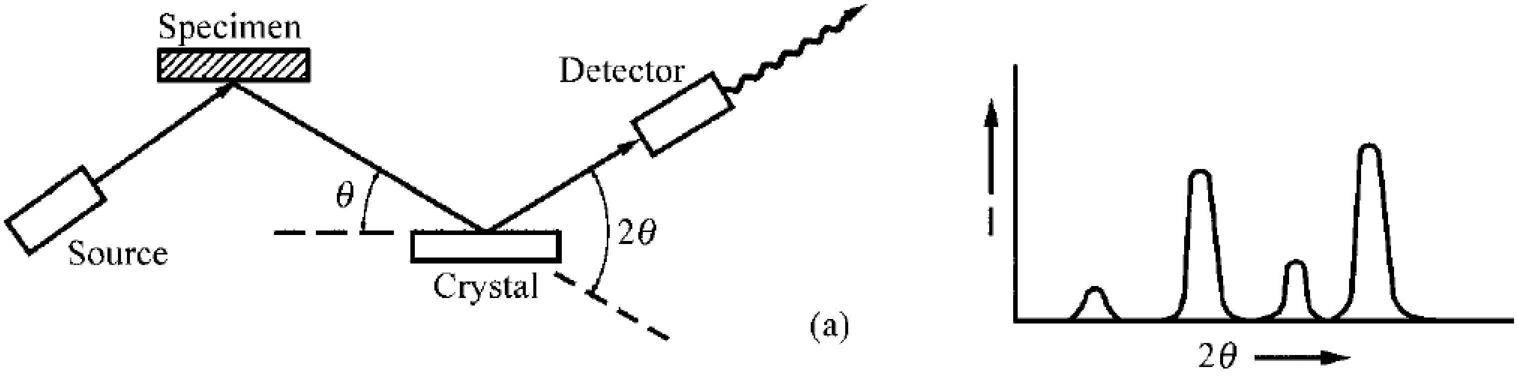
Energy dispersive spectroscopy (EDS)

XRF is a fast, accurate and non-destructive material characterization method that requires small amount of sample

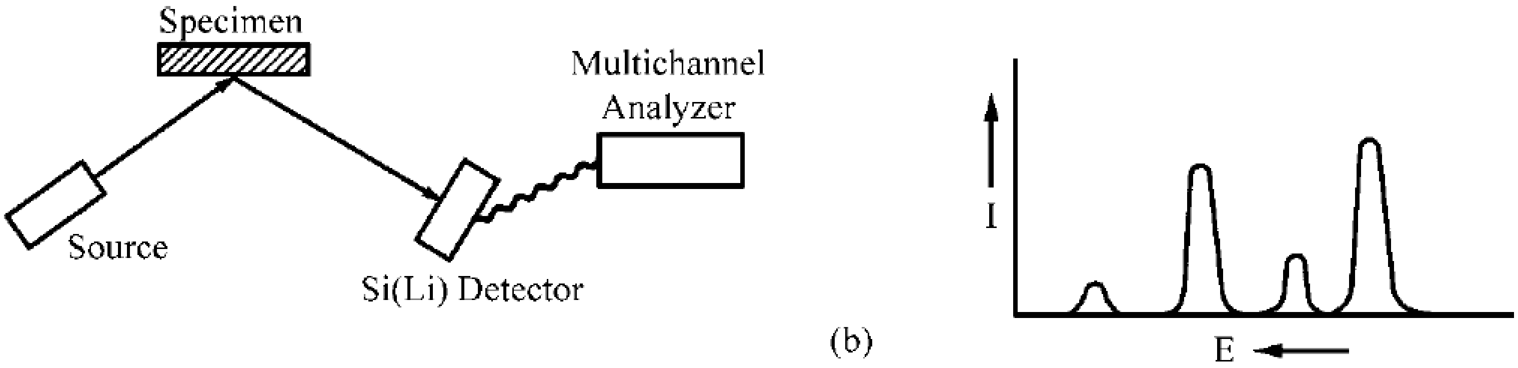
Measurement time varies between seconds and about 30 minutes per sample depending on the number of determined elements

The quantitative analysis based on measurement results takes seconds to complete

WDS
(WDXRF)



EDS
(EDXRF)



A typical XRF consists of 3 components:

- X-ray source (The same as in XRD, power of 0.5 – 3 kW and voltage of 30 – 50 kV. Typical anode materials are Cr, Rh, W, Ag, Au and Mo)
- X-ray detector
- Data acquisition and processing system

WDS and EDS based XRF devices differ due to their X-ray detectors

WDS method utilizes a single crystal to diffract the characteristic X-rays that are fluoresced from the sample, according to the Bragg's law

EDS method utilizes a photon detector (typically a Si(Li) diode) to sort fluoresced photons according to their energies

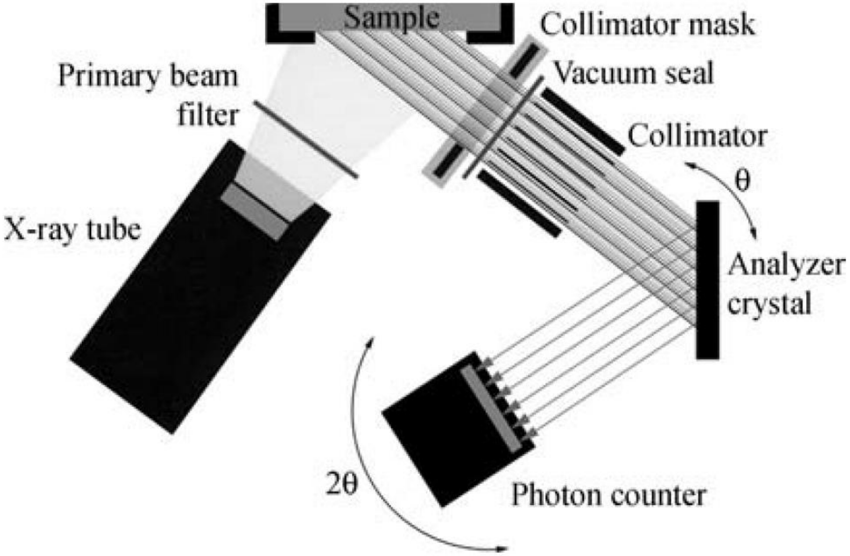
WDS (Wavelength Dispersive Spectroscopy)

XRF technique was invented based on the WDS in 1950s

Compared to the much simple EDS set-up, WDS provides higher resolution and elemental analysis for a wider atomic number range

WDS systems are capable of resolving the ($\Delta\lambda/\lambda$) at a resolution between 0.002-0.02 A and analyzing elements with atomic number greater than 6 (C and higher)

WDS systems are very similar to XRD in operating principles

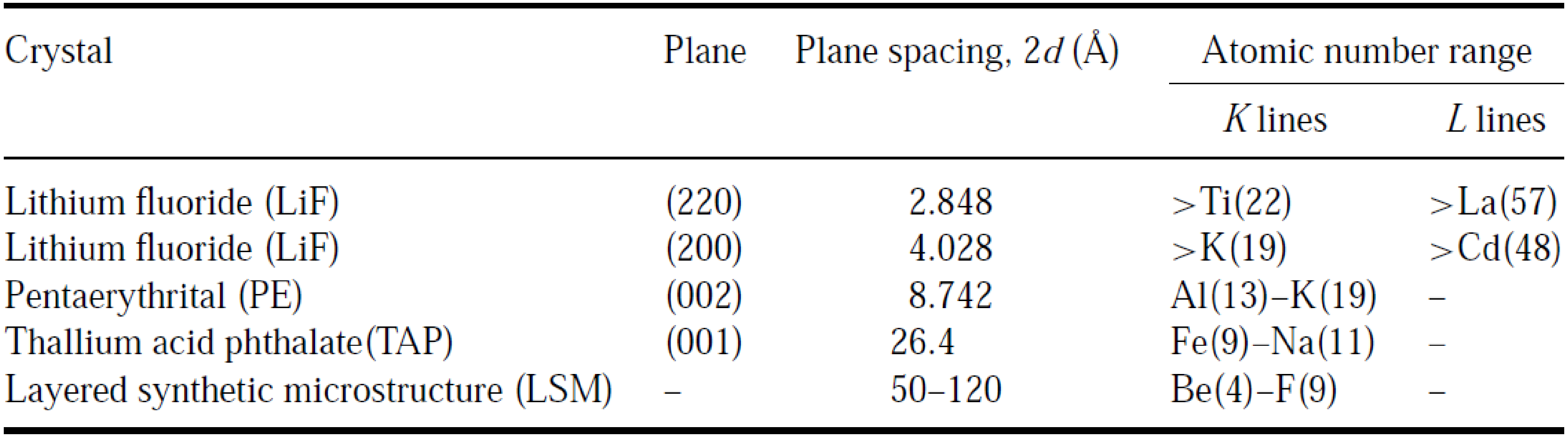


WDS

The analysis crystal type is of high importance as it determines the range of detectable atomic numbers

Bragg law is used to calculate the wavelength range that are detectable by a crystal

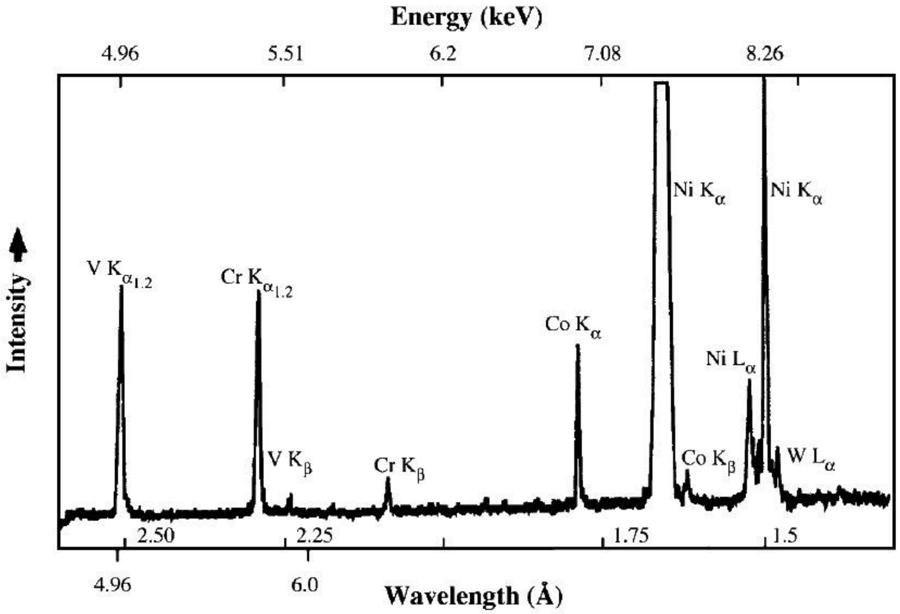
A maximum θ degree of 73 is applicable



Crystal	Plane	Plane spacing, 2*d* (Å)	Atomic number range	
			K lines	*L* lines
Lithium fluoride (LiF)	(220)	2.848	>Ti(22)	>La(57)
Lithium fluoride (LiF)	(200)	4.028	>K(19)	>Cd(48)
Pentaerythrital (PE)	(002)	8.742	Al(13)–K(19)	–
Thallium acid phthalate(TAP)	(001)	26.4	Fe(9)–Na(11)	–
Layered synthetic microstructure (LSM)	–	50–120	Be(4)–F(9)	–

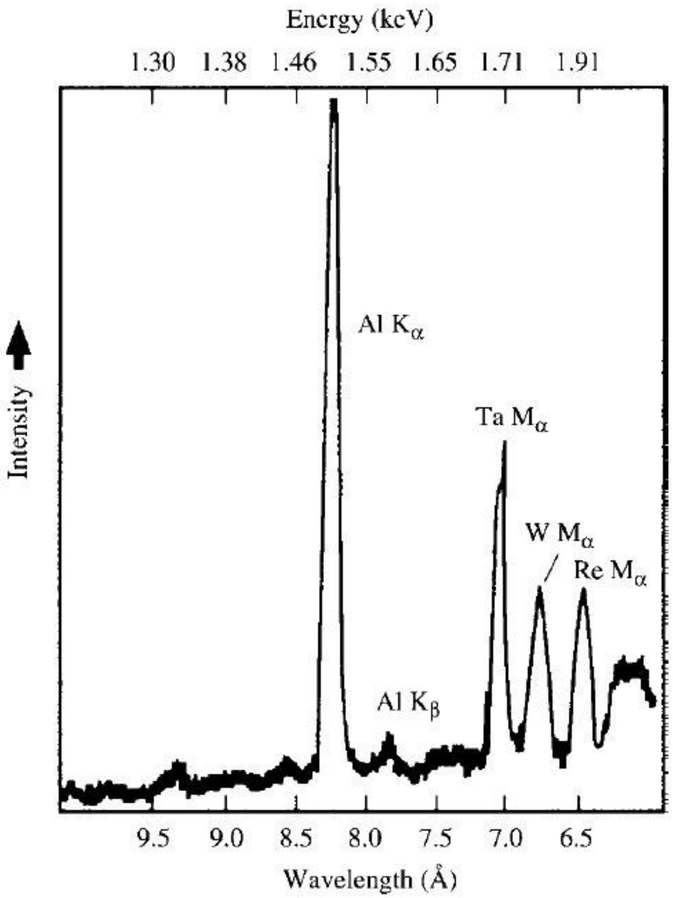
WDS

Each peak in a WDS spectrum represents the characteristic fluorescence of the related element. The relative intensity of the diffracted characteristic X-rays are shown in the y-axis

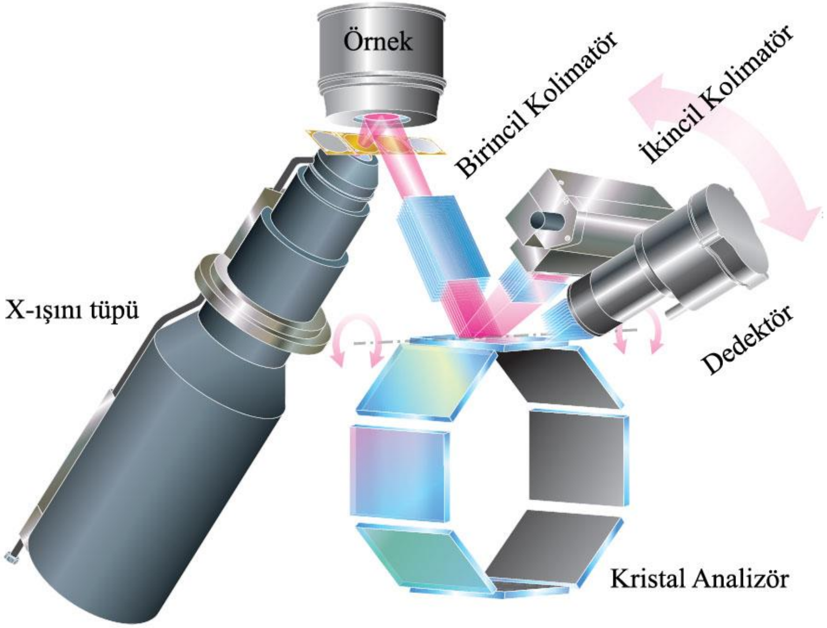


WDS

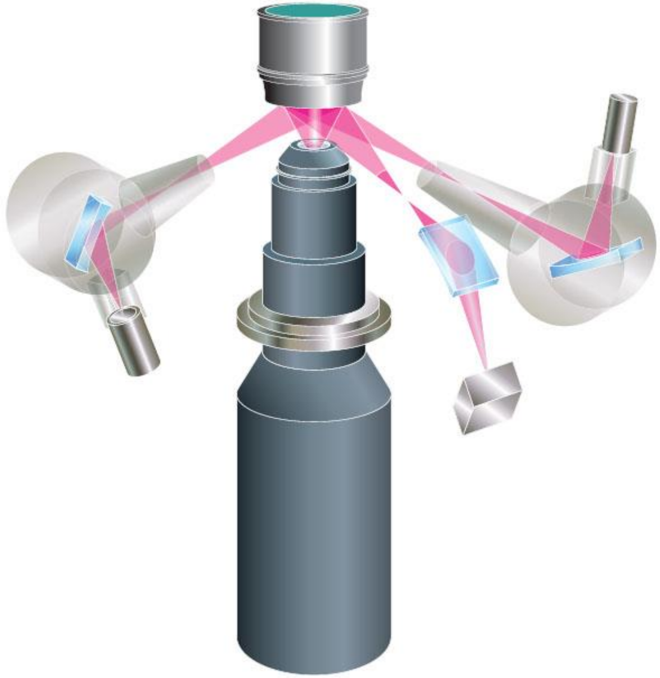
More than one crystal may be used to analyze all the fluorescent X-rays from one sample (LiF and TAP crystals are utilized to obtain spectrum from a Nickel alloy in the figure)



WDS **(Wavelength Dispersive Spectroscopy)**



WDXRF system with a direct diffracting 2D optical system



Simultaneous WDXRF with different diffracting crystals and detecting systems for analysis of different elements

EDS
Energy Dispersive Spectroscopy

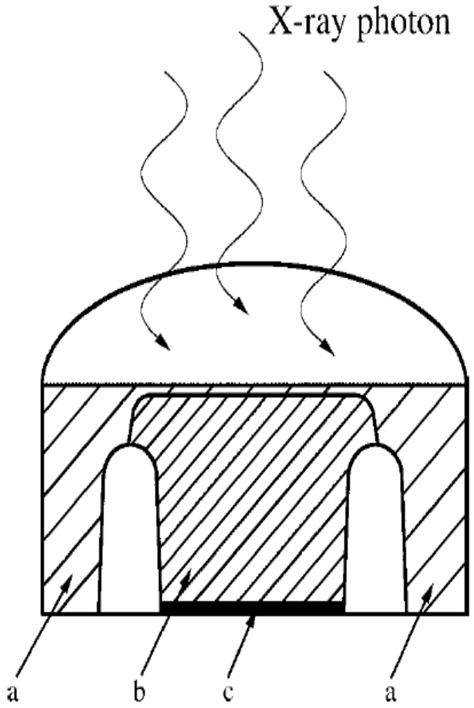
Si(Li) detector is used in a typical EDS system. This detector is composed of a small cylinder of p-type Si and Li, combined in the form of a diode.

X-ray photons collected by the detector produce a pair of electron gaps. These photons have to have an average energy to produce electron gap pairs in Si(Li) diodes.

More pairs result from higher energy photons.

Characteristic X-rays are sorted according to their energies.

X-ray photons pass through a very thin (10 μm) beryllium window before hitting the detector

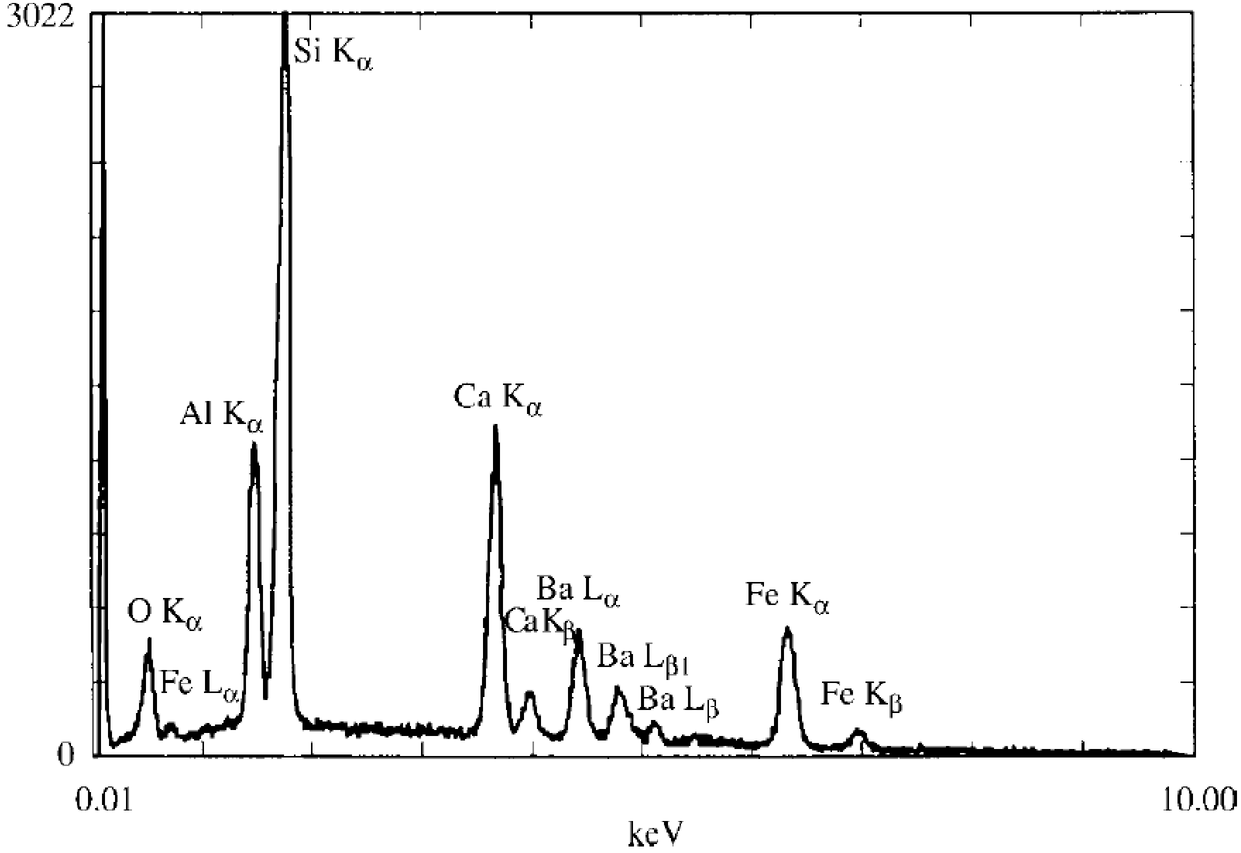


A: P-tipi silisyum

B: lityum bölgesi

C: n-tipi silisyum

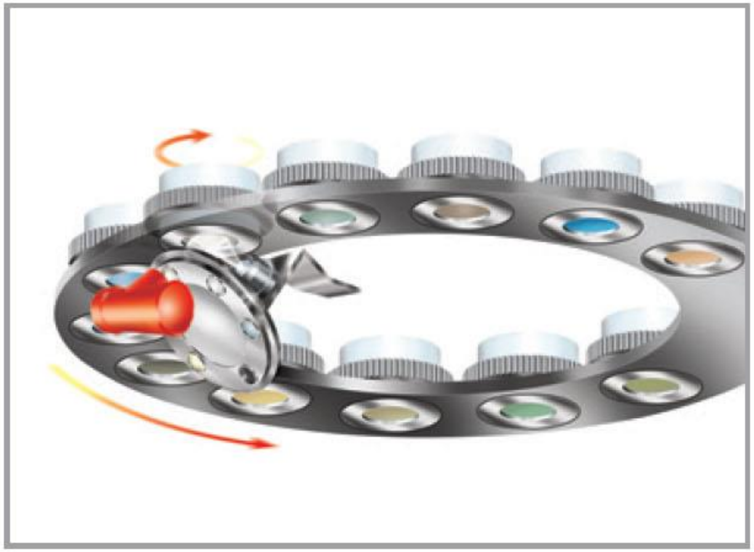
EDS Spectrum



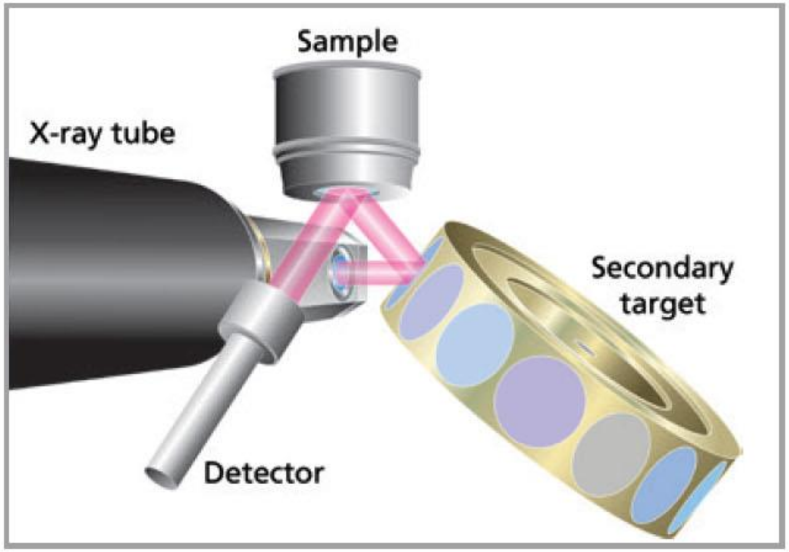
EDS analysis of glass

EDXRF Geometry

- There are 2 fundamental spectroscopes: 2D and 3D
- They both contain an X-ray source and EDS



2D optik sistemli

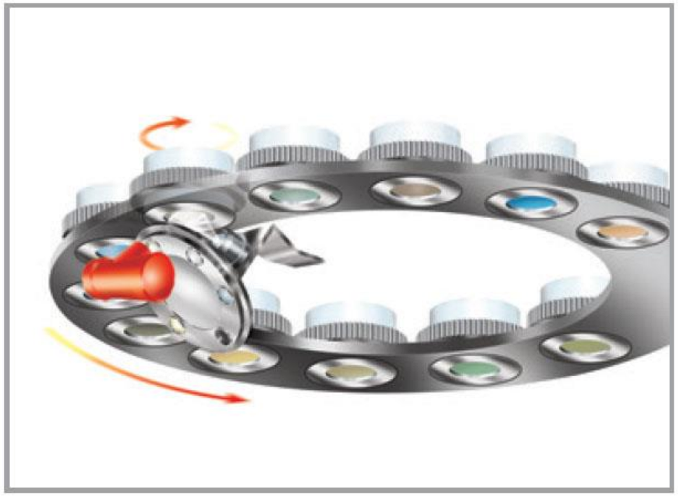


3D optik sistemli

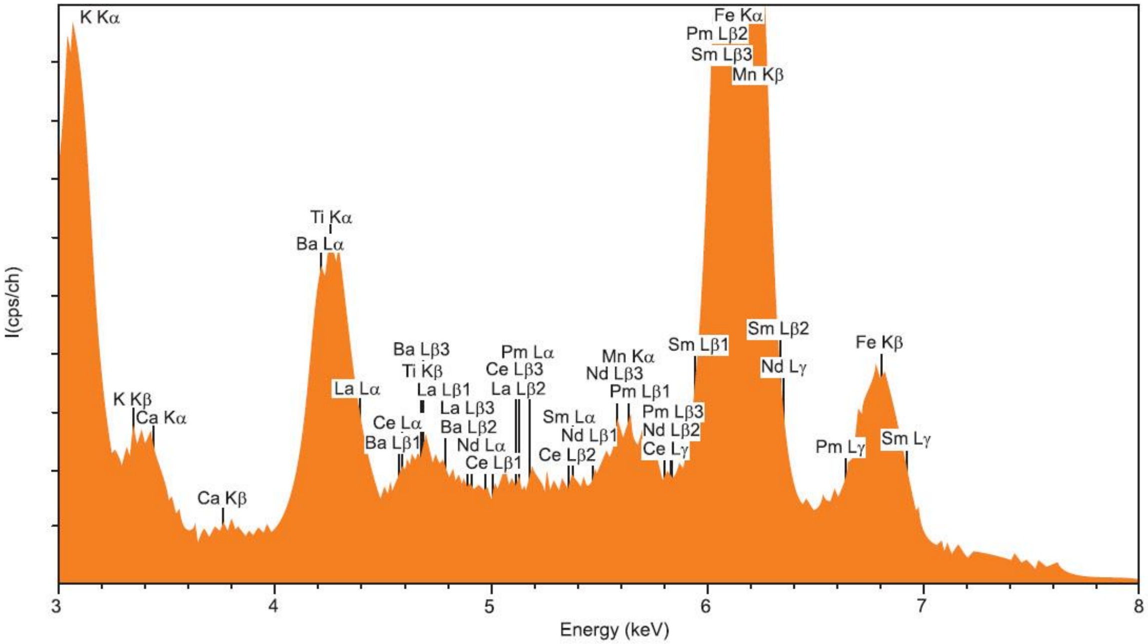
EDS(EDXRF) spectroscope with 2D optical system

- X-ray photons that are emitted from the source are directed towards the sample and the fluorescent photons are directed to the detector
- In this setup the detector receives both the fluorescent photons and the photons emitted from the source which produce noise in the spectrum. This makes identification of trace elements with small peaks difficult.

Direct emission in a 2D optical system



EDS(EDXRF) spectroscopy with 2D optical system



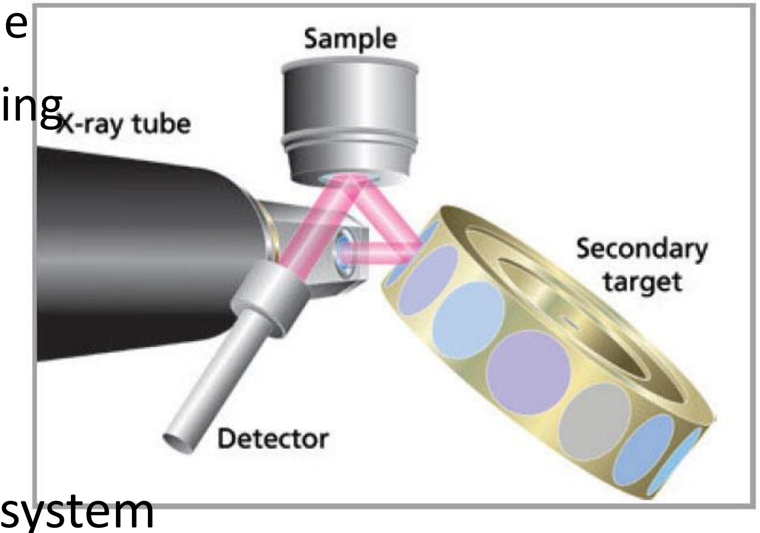
EDXRF spectrum of soil

EDS(EDXRF) spectroscopy with 3D optical system

- X-rays emitted from the source are directed through two planes that are oriented across each other. X-rays are sent to a secondary target which converts them to monochromatic photons that are directed towards the sample
- This setup has the advantage of preventing the

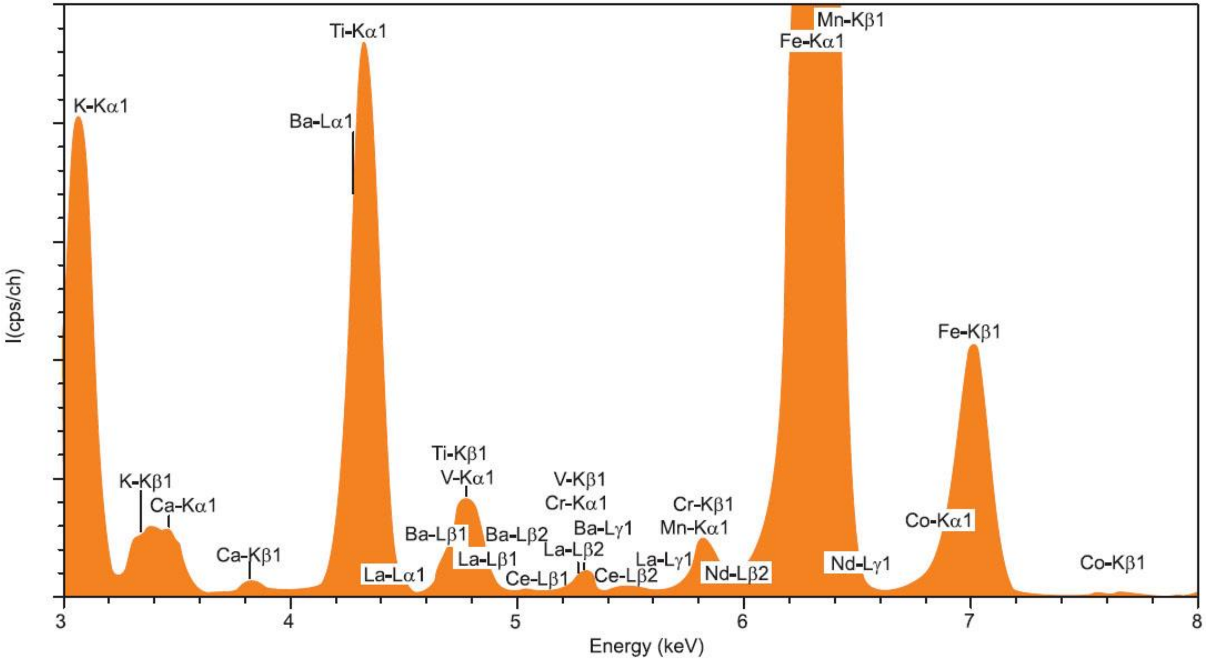
Primary X-rays from reaching the detector resulting

in a very low noise



Indirect emission in a 3D optical system

EDS(EDXRF) spectroscopy with 3D optical system



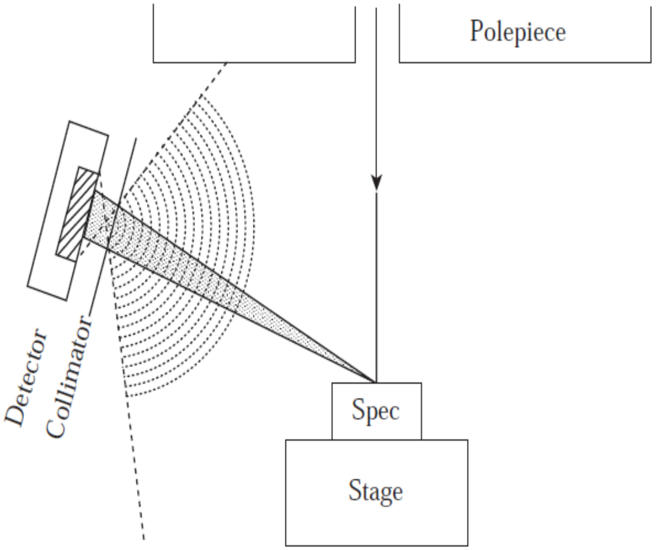
EDXRF spectrum of soil using 3D optical system

EDS detector in the SEM

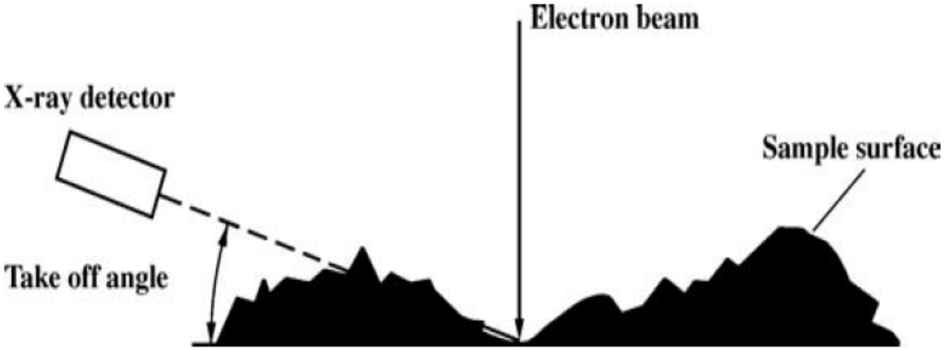
- EDS detectors are integrated into the SEM and TEM because they are simpler than WDS. This setup enables elemental analysis during microstructural analysis.

The main difference between the EDXRF and the EDS in SEM is the mechanism of fluorescence from the sample. A high energy electron beam is used in SEM EDS to generate fluorescence.

EDS detector in the SEM

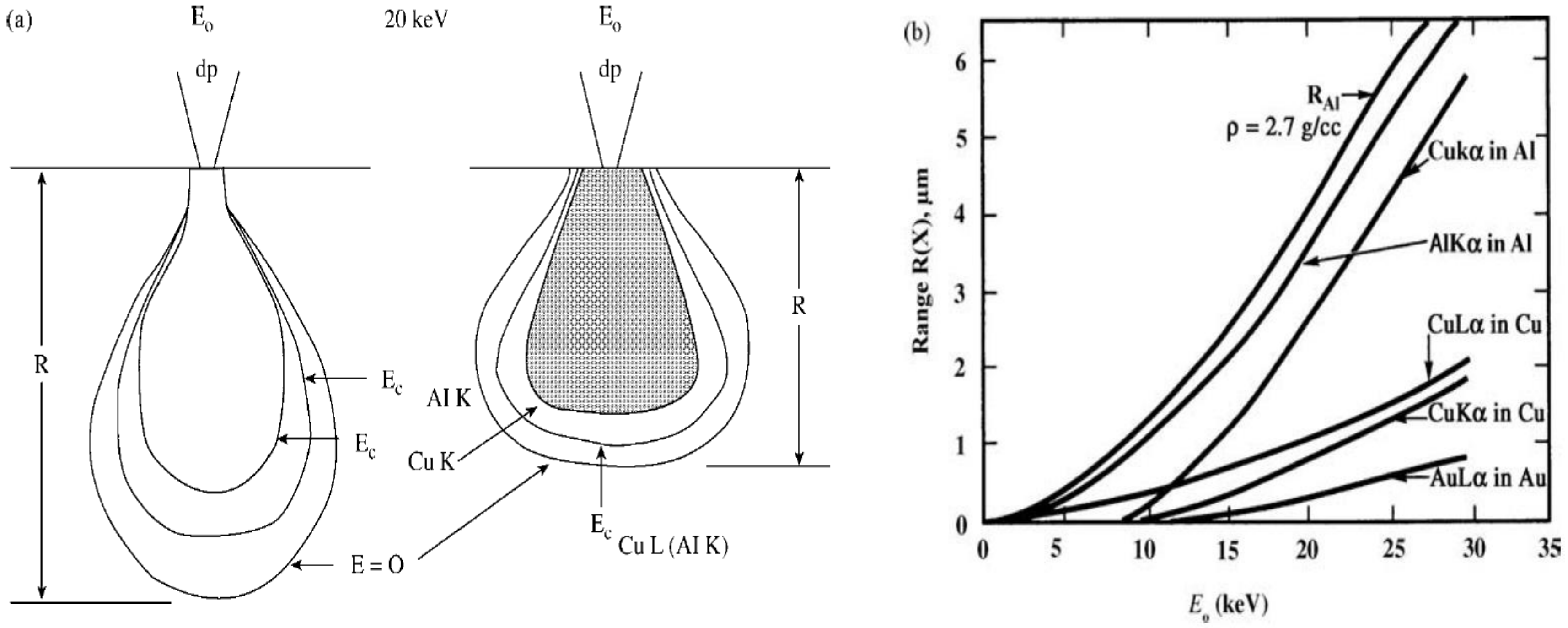


EDS setup in a TEM

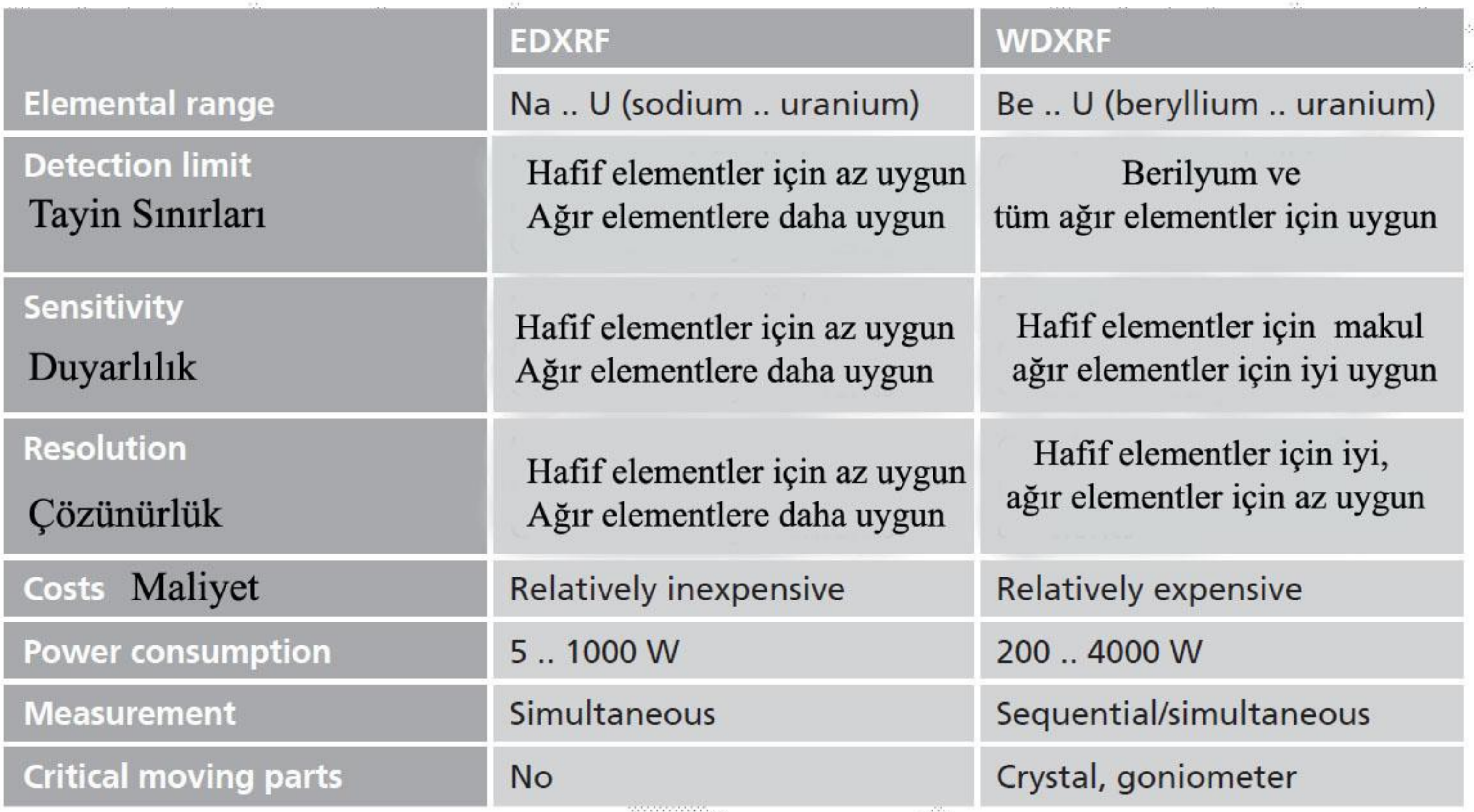


Orientation of the X-ray detector for rough surface analysis

X-ray fluorescence zones from samples with different atomic numbers

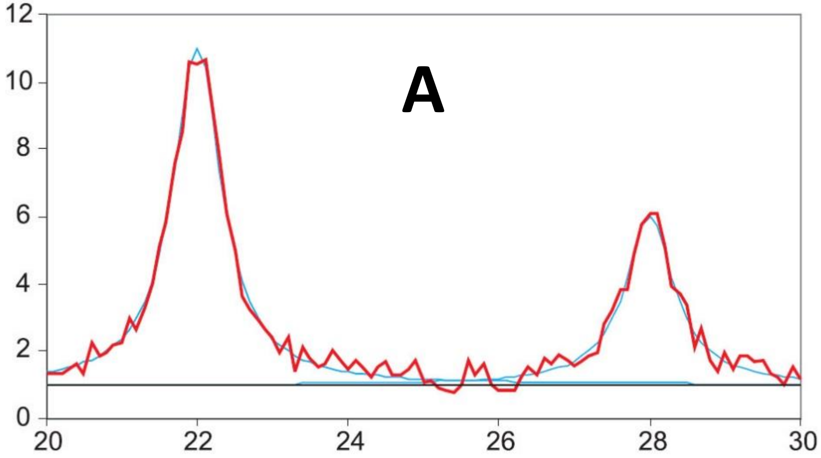


Comparison of WDXRF and EDXRF Techniques

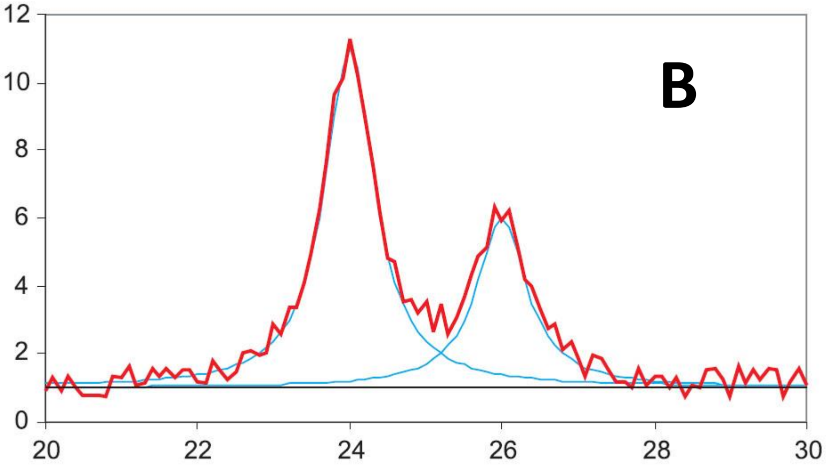


	EDXRF	WDXRF
Elemental range	Na .. U (sodium .. uranium)	Be .. U (beryllium .. uranium)
Detection limit Tayin Sınırları	Hafif elementler için az uygun Ağır elementlere daha uygun	Berilyum ve tüm ağır elementler için uygun
Sensitivity Duyarlılık	Hafif elementler için az uygun Ağır elementlere daha uygun	Hafif elementler için makul ağır elementler için iyi uygun
Resolution Çözünürlük	Hafif elementler için az uygun Ağır elementlere daha uygun	Hafif elementler için iyi, ağır elementler için az uygun
Costs Maliyet	Relatively inexpensive	Relatively expensive
Power consumption	5 .. 1000 W	200 .. 4000 W
Measurement	Simultaneous	Sequential/simultaneous
Critical moving parts	No	Crystal, goniometer

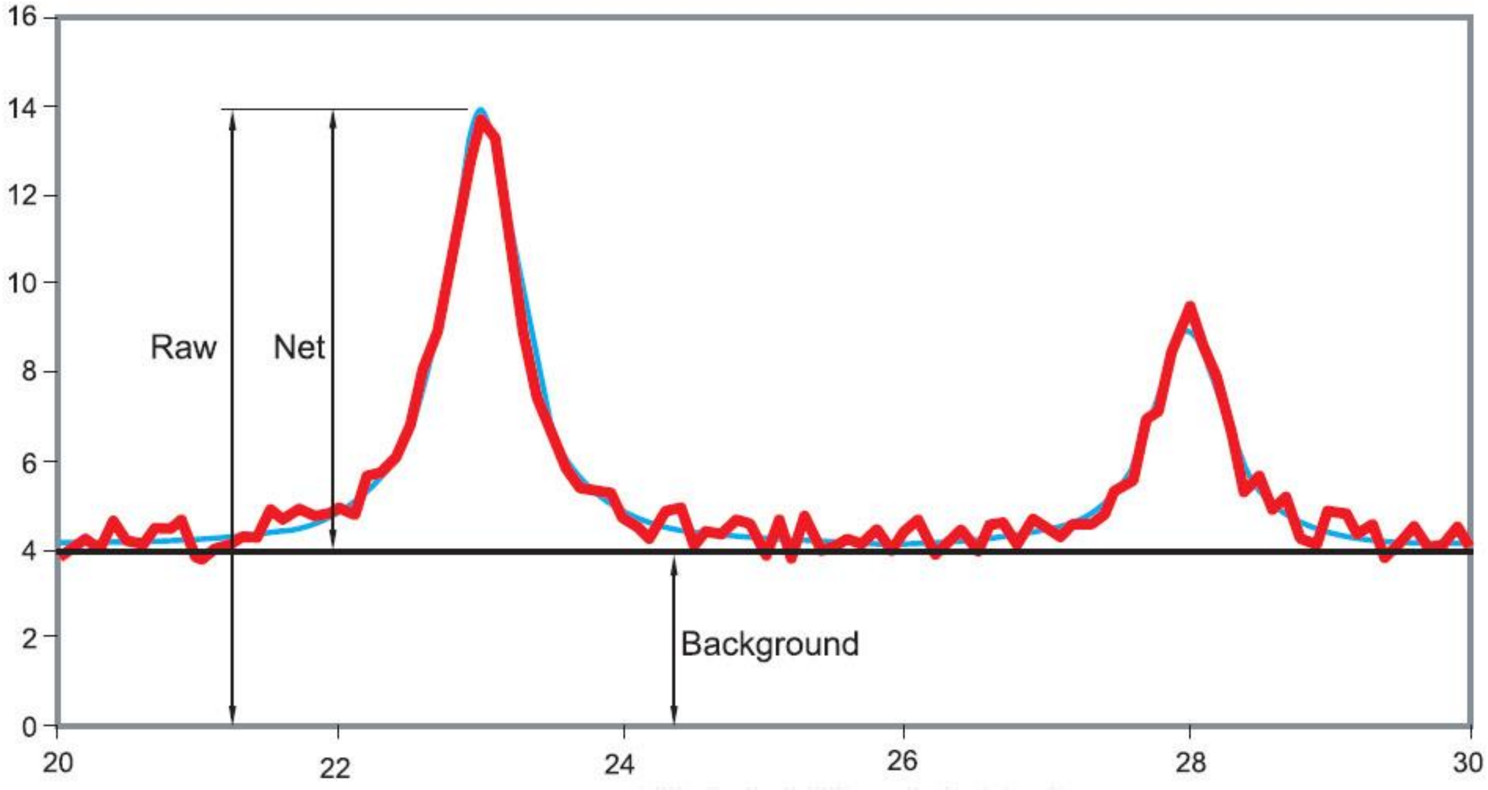
Background and profile corrections



Background correction for two separate peaks

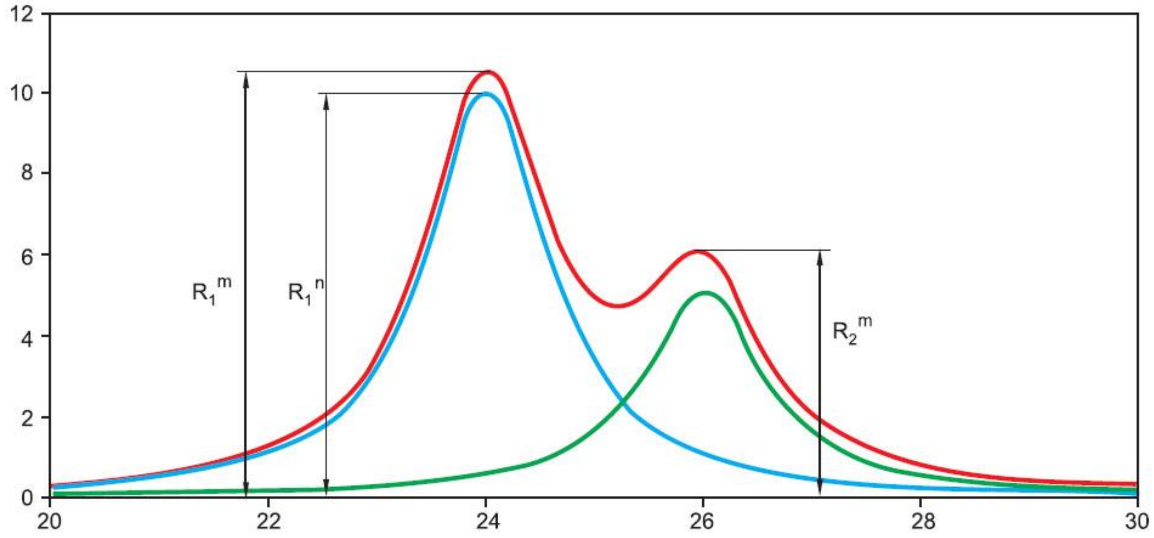


Background correction and peak profiling for two overlapping peaks



Peak intensity measurement and background correction

Peak overlapping and correction



$$R_1^m = R_1^n + f_{12} \cdot R_2^n$$

$$R_2^m = f_{21} \cdot R_1^n + R_2^n$$

$$f_{12} = \frac{R_{2,1}}{R_2}$$

Overlap factor

Quantitative analysis using EDXRF ve WDXRF

- Intensity in EDXRF is obtained from peak area while peak height is used for intensity measurement in WDXRF
- After a few calibration runs, the device converts relative peak intensities into quantities
- Peak intensity in the spectrum does not only depend on the concentration of the original element but also on the number and intensities of other elements
- Presence of other elements may weaken or strengthen the intensity

Quantitative analysis with EDXRF ve WDXRF Techniques

$$X = M * K * I_R$$

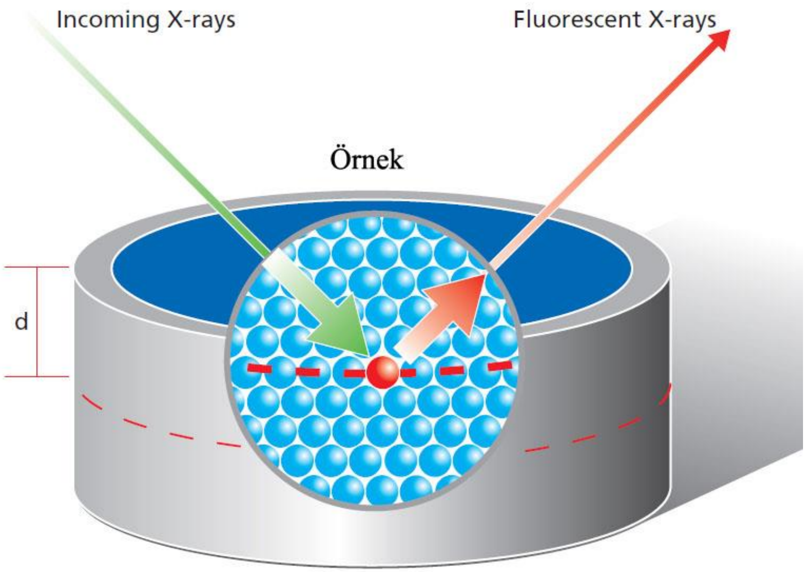
Weight fraction of an element (X) is proportional to its relative intensity (I_R) by the instrument factor (K) and the sample matrix factor (M).

K is related to the condition of the source, emission and geometric position of the sample

M contains 3 basic matrix factors:

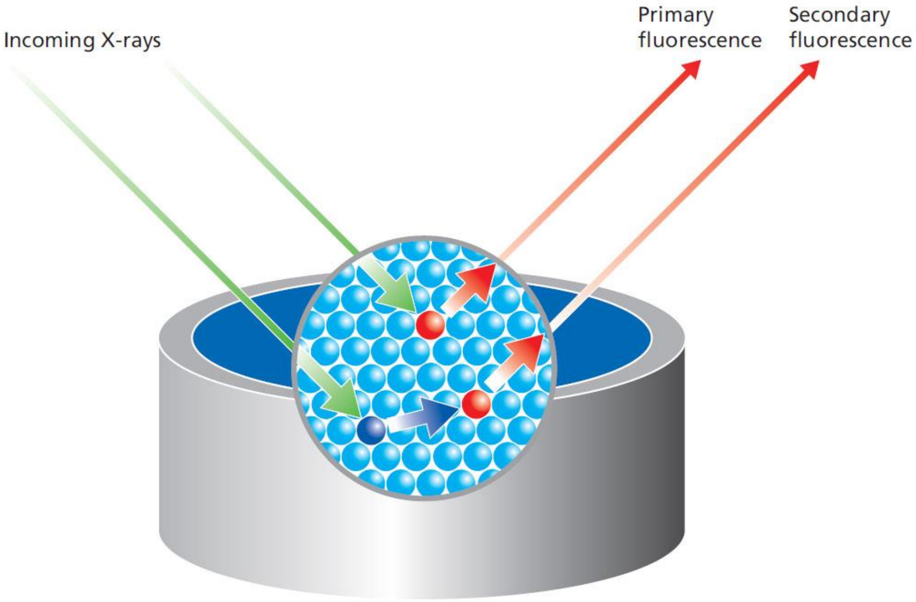
1. Absorption of the X-ray by the sample
2. Secondary absorption
3. Secondary fluorescence

A



Absorption by the sample

B



Strengthening of the intensity of one element by the secondary fluorescence of another element