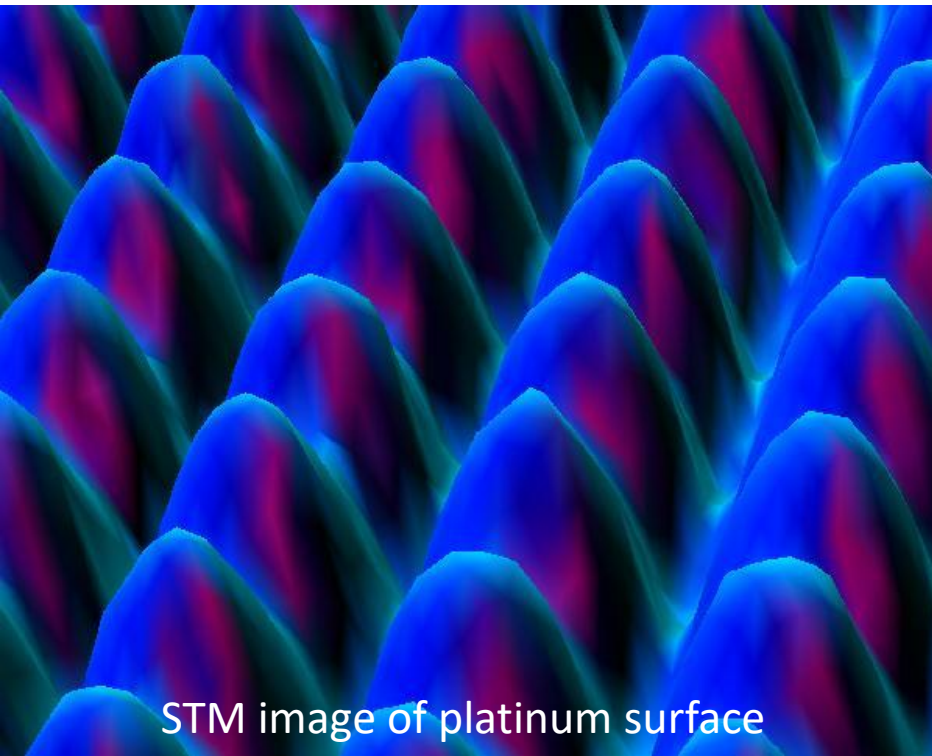


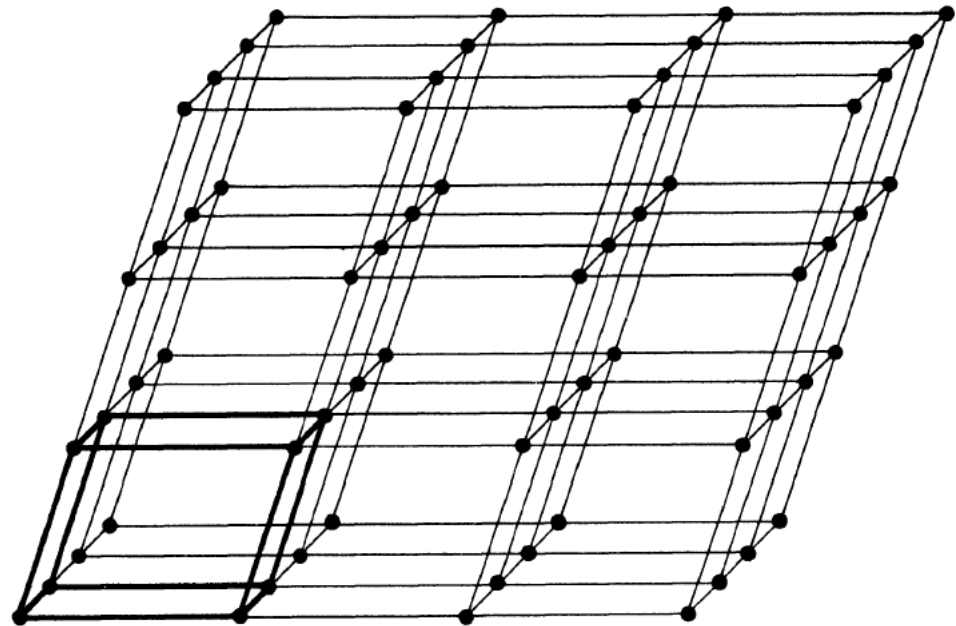
X-ray Techniques for Crystallinity Analysis

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 Haüy** (1743 – 1822).

Haüy, 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 cristaux***, based on the unit of the compound **molécule intégrante**, specific in shape and composition for every compound.



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:

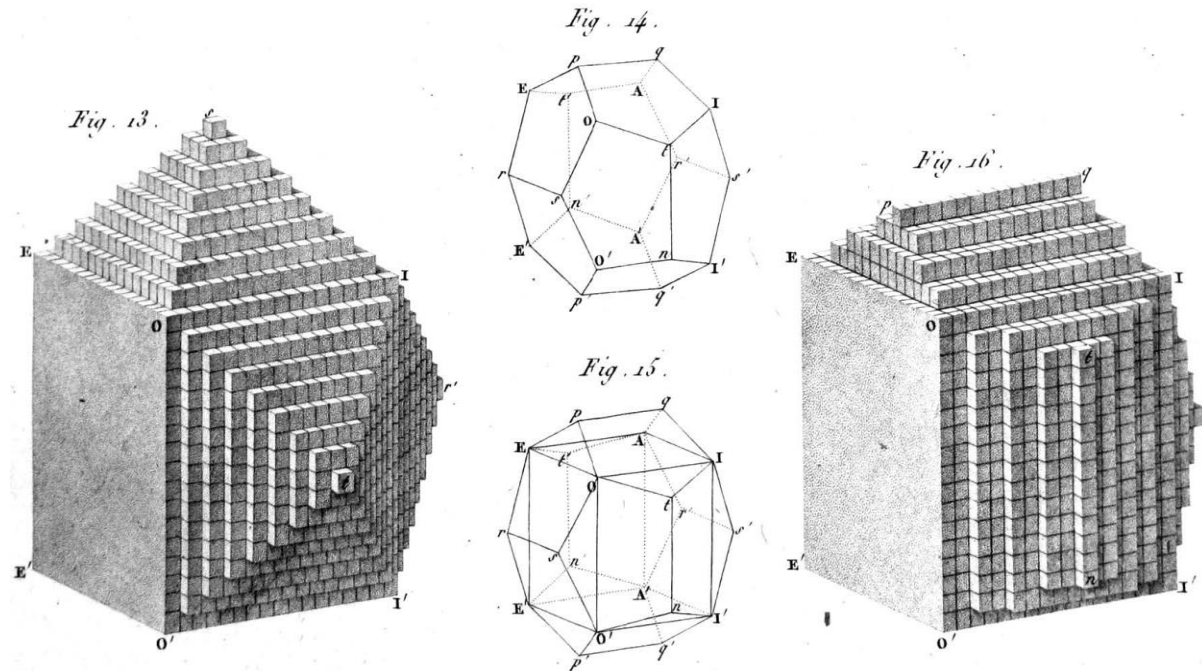
cubic *molécules intégrantes*,
cubic primitive form

simple decrement

rhomb-dodecahedron (Fig. 13)

complex decrements

pentagon-dodecahedron (Fig. 16)



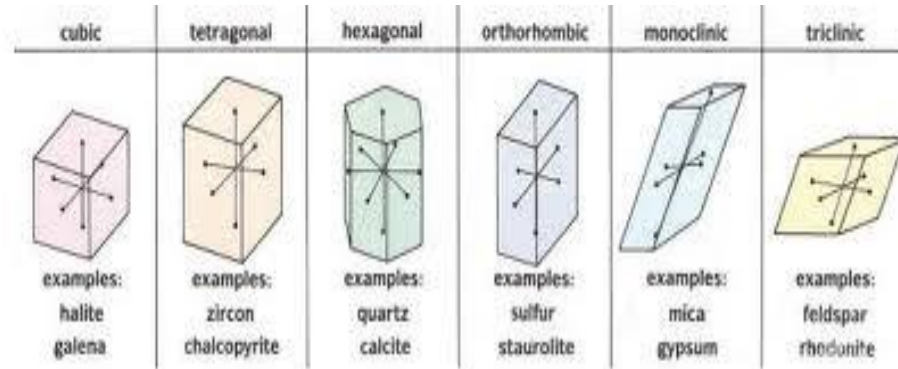
Crystalline Symmetry & Systems

The over-riding focus in 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.

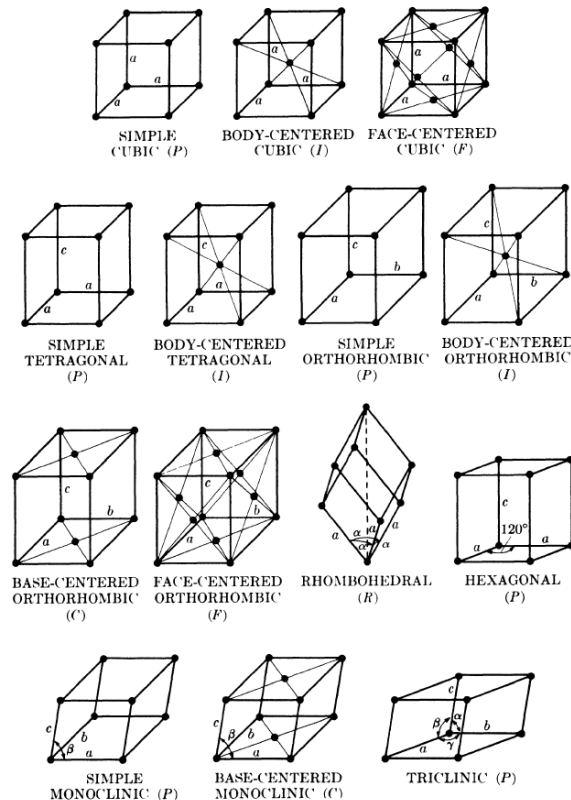
Influence of German **Naturphilosophie**.

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

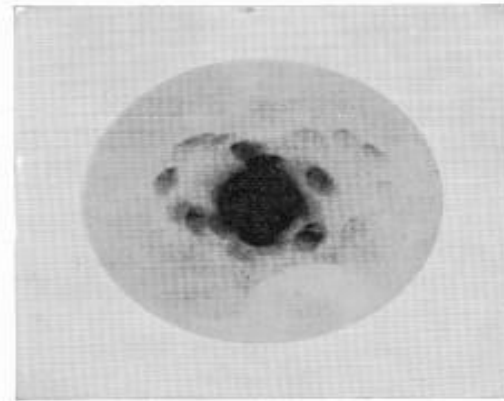


Fig. 4-4(1). Friedrich & Knipping's first successful diffraction photograph.

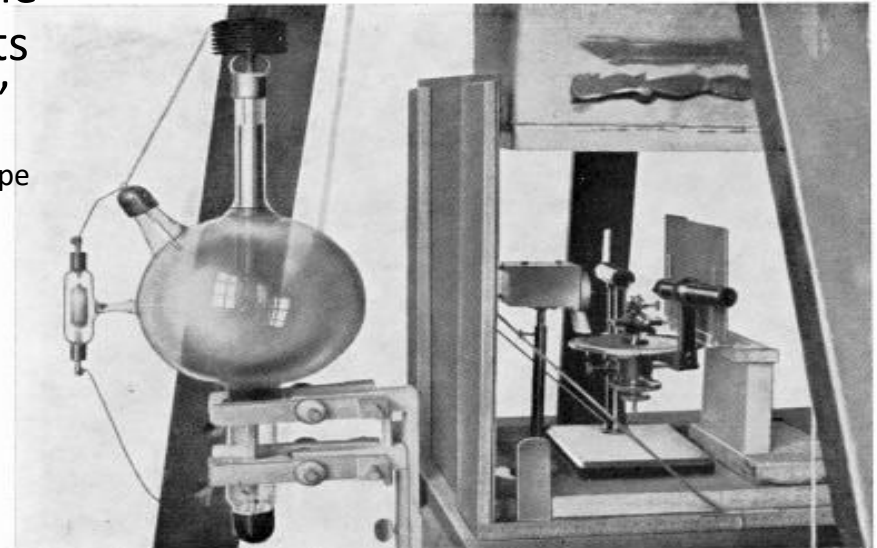


Fig. 4-4(2). Friedrich & Knipping's improved set-up.

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.

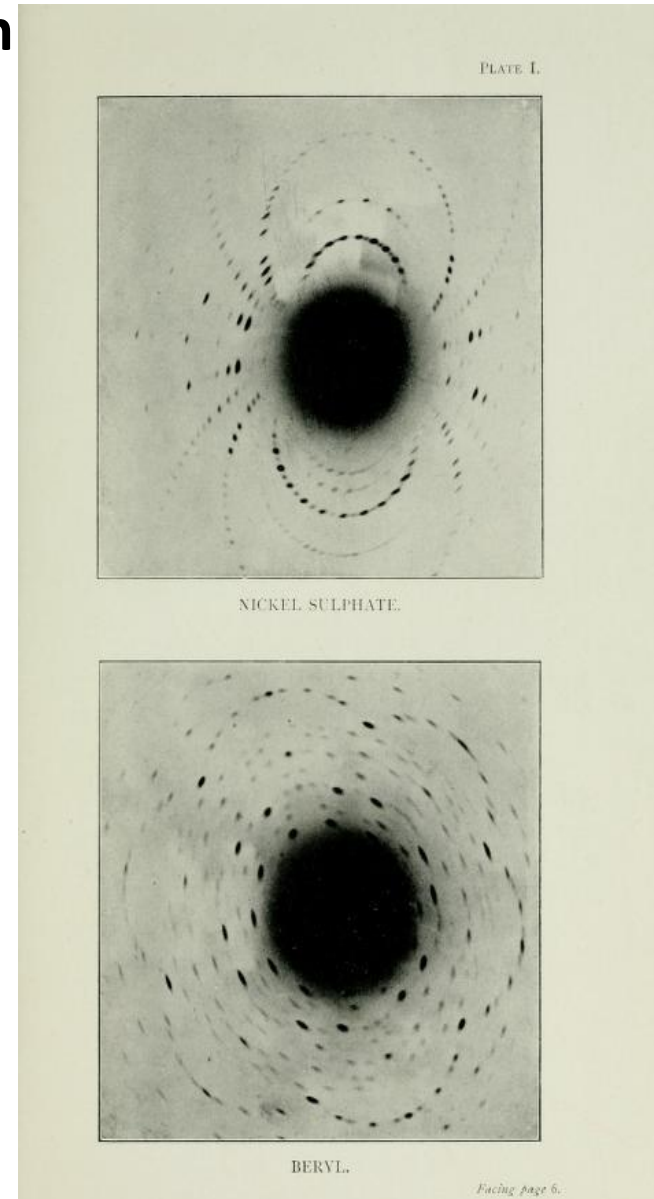
He thereby devised **Bragg's Law.**, $n\lambda=2d\sin\theta$.

*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.

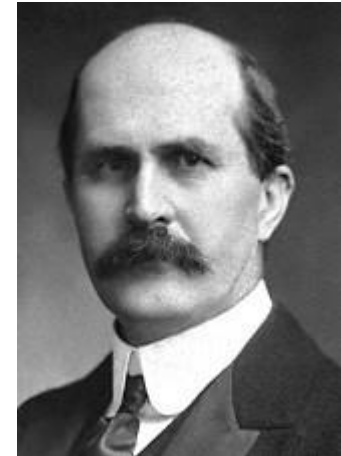
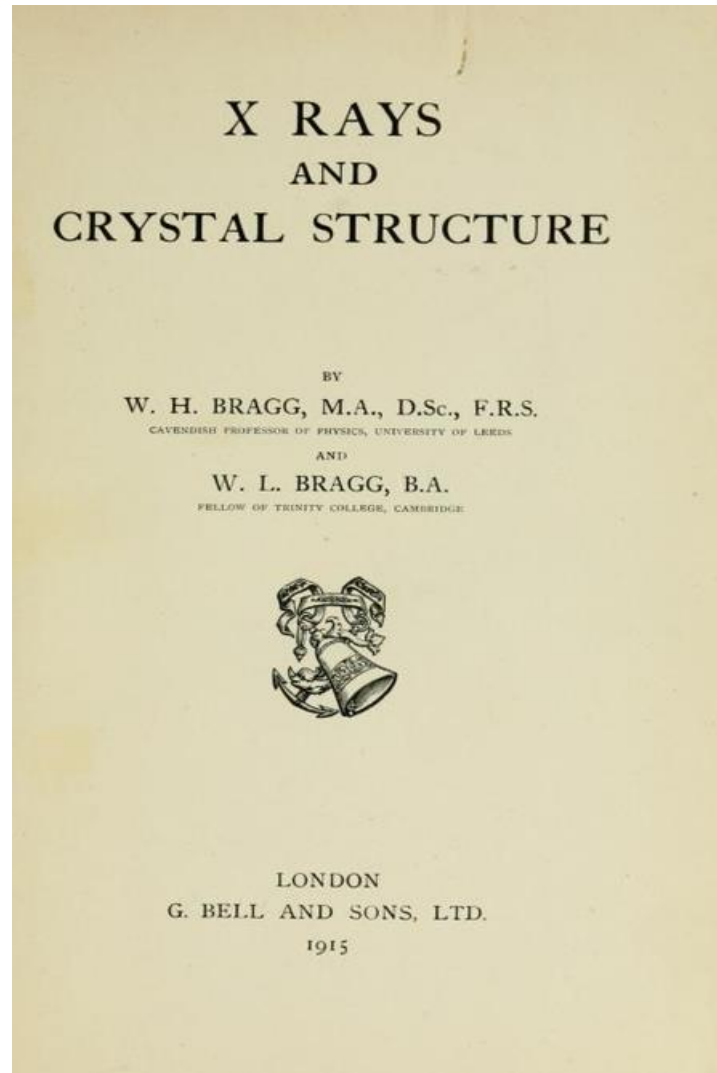
W.H. & W. L. Bragg, X-Rays and Crystal Structure (1915)

“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).



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



Photos

Top: William Henry Bragg
(1862 – 1942);

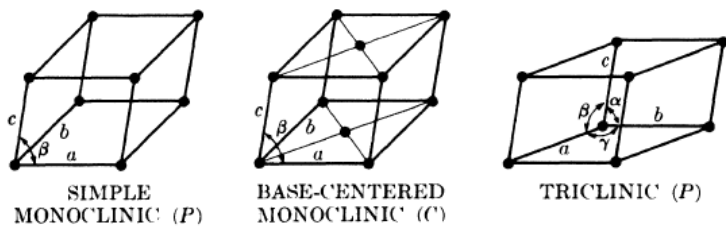
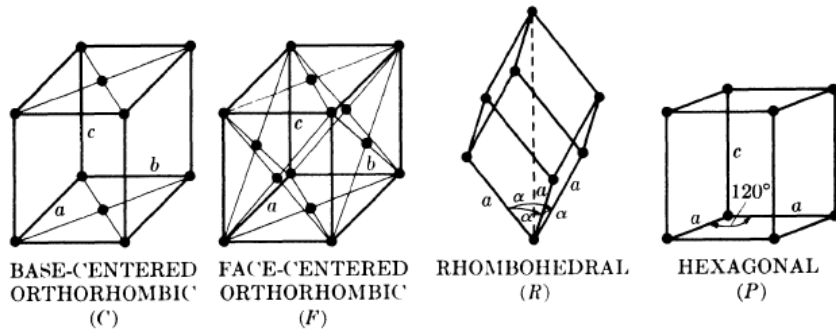
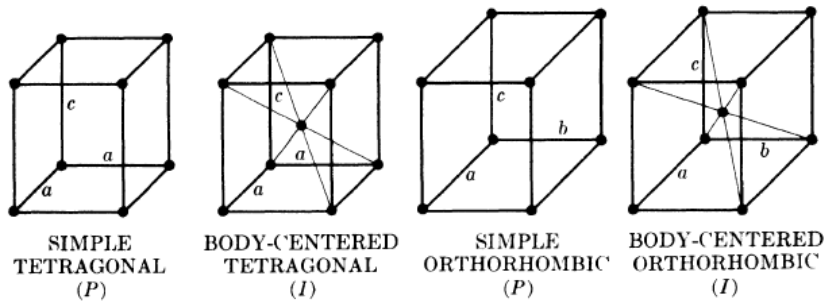
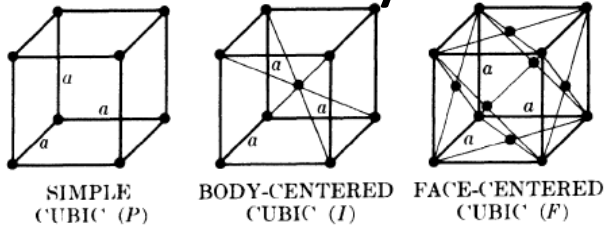
Bottom William Lawrence
Bragg

(1890-1971)

Swedish postage stamp
with Braggs

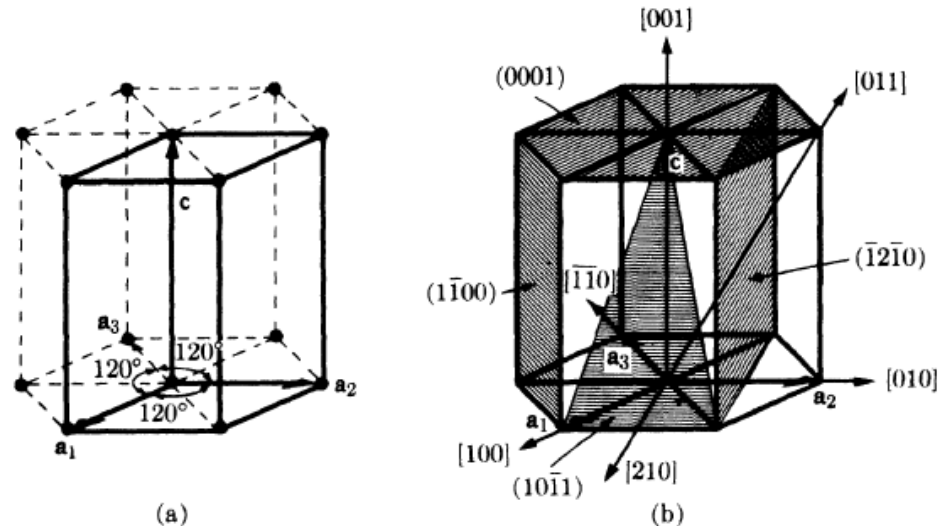


Geometry of Crystals



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.



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

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.

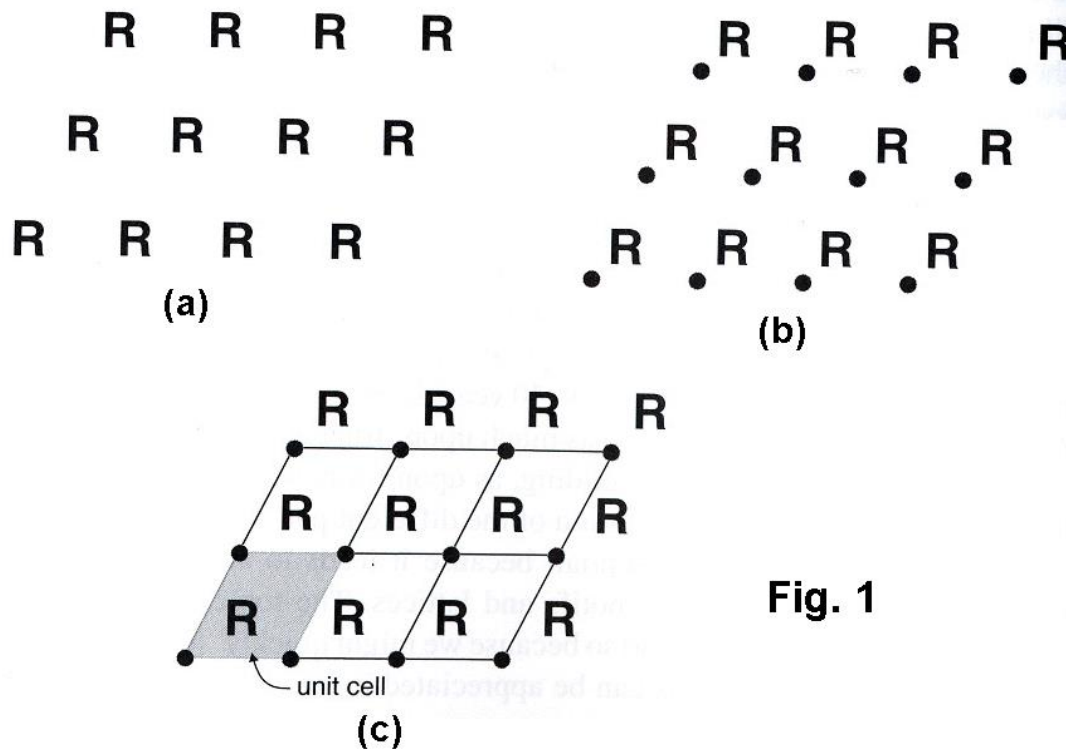


Fig. 1

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.

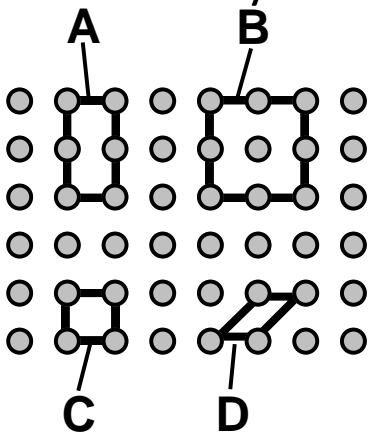


Fig. 2

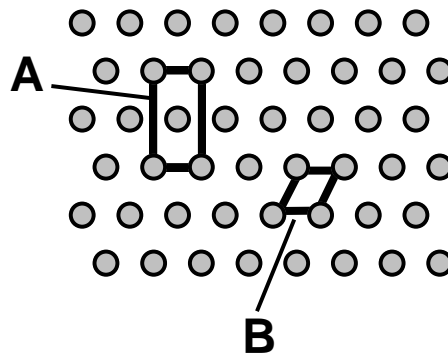
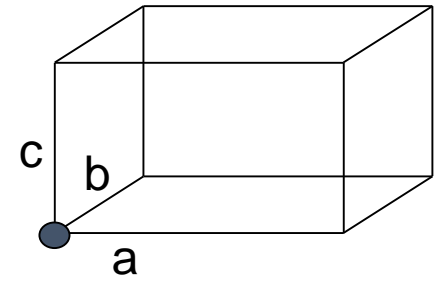


Fig. 3

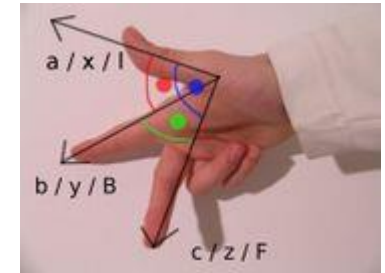
There is no unique way of choosing a unit cell. For example, each of the cells (A to D) in Fig. 2 are OK. However, the cell favoured by crystallographers is the one of smallest volume that displays all of the symmetry of the lattice. Thus, cells C and A are the preferred unit cells for the lattices of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

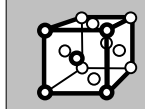
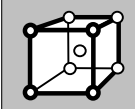
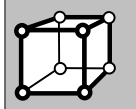
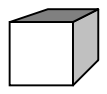


In general, six parameters are required to define the shape and size of a unit cell, these being three cell edge lengths (conventionally, defined as a , b , and c), and three angles (conventionally, defined as α , β , and γ). In the strict mathematical sense, a , b , and c are vectors since they specify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

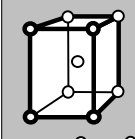
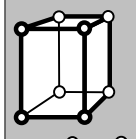
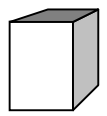
α is the angle between b and c , β is the angle between a and c , γ is the angle between a and b . The unit cell should be right handed. Check the cell above with your right hand

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

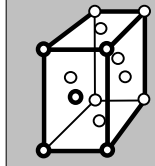
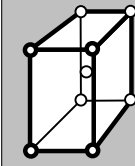
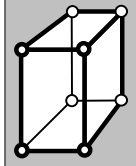
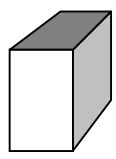
Cubic



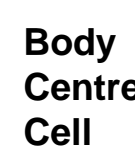
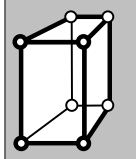
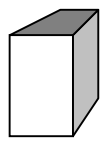
Tetragonal



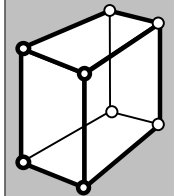
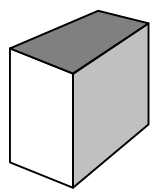
Orthorhombic



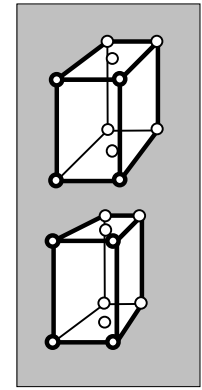
Monoclinic



Triclinic

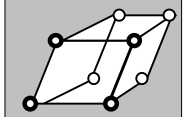
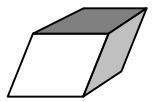


End Face Centred Cell

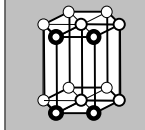
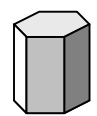


C

Trigonal



Hexagonal



Primitive Cell
P

Body Centred Cell
I

Face Centred Cell
F

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.

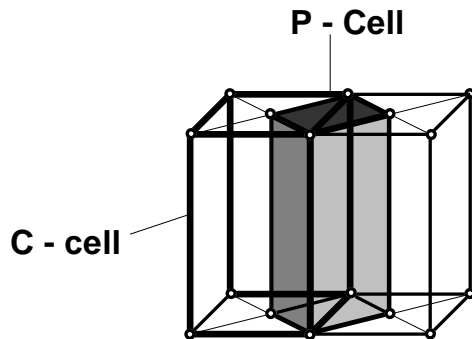


Fig. 4

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

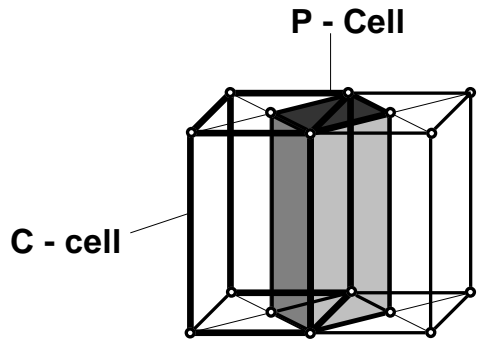
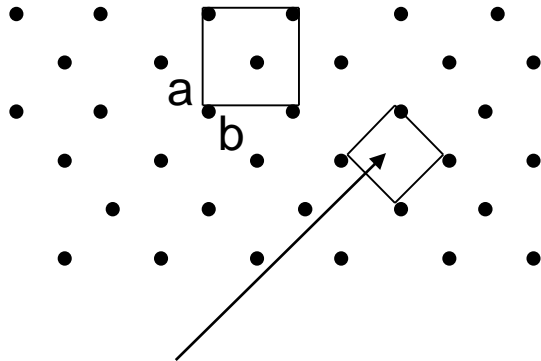


Fig. 4

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

Tetragonal

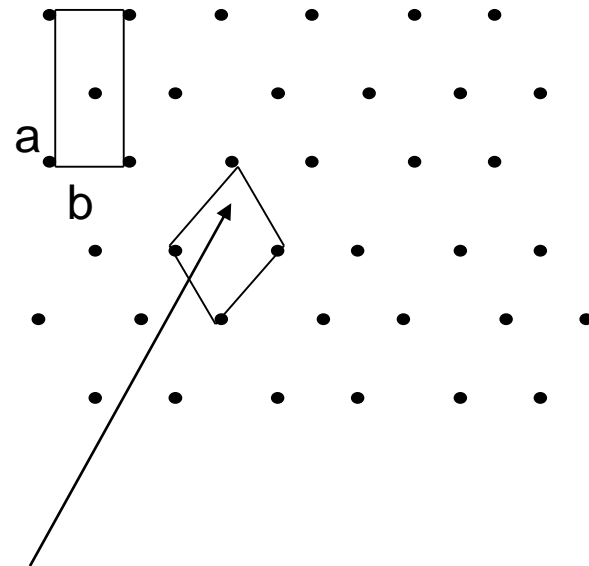
$$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$$



Smaller cell is Tetragonal P

Orthorhombic

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



Angle not 90° 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

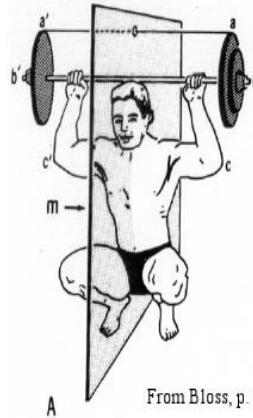
Symmetry Elements and Operations

“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.

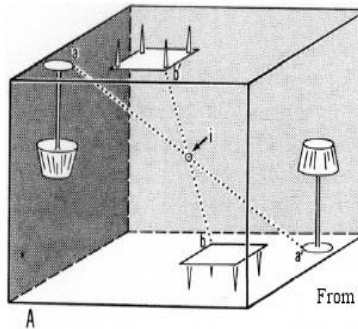
Symmetry Operations ---} 32 Point Groups

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



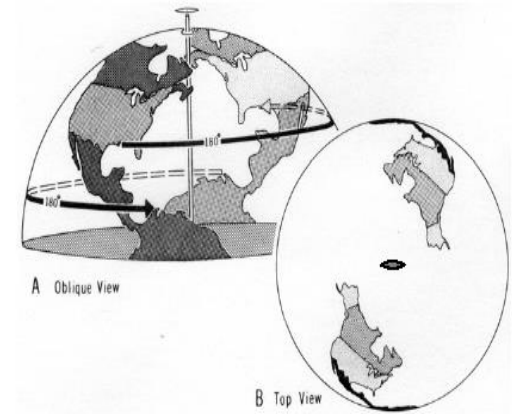
From Bloss, p. 2

2. REFLECTION = m



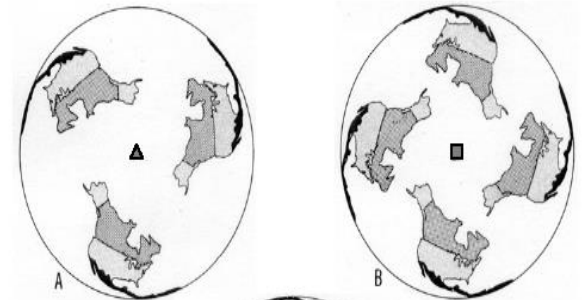
From Bloss, p. 6

4. INVERSION = i



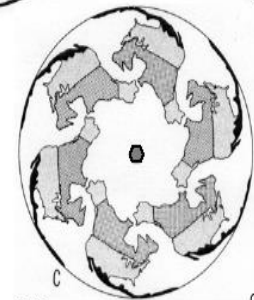
A Oblique View

B Top View



A

B



C

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.

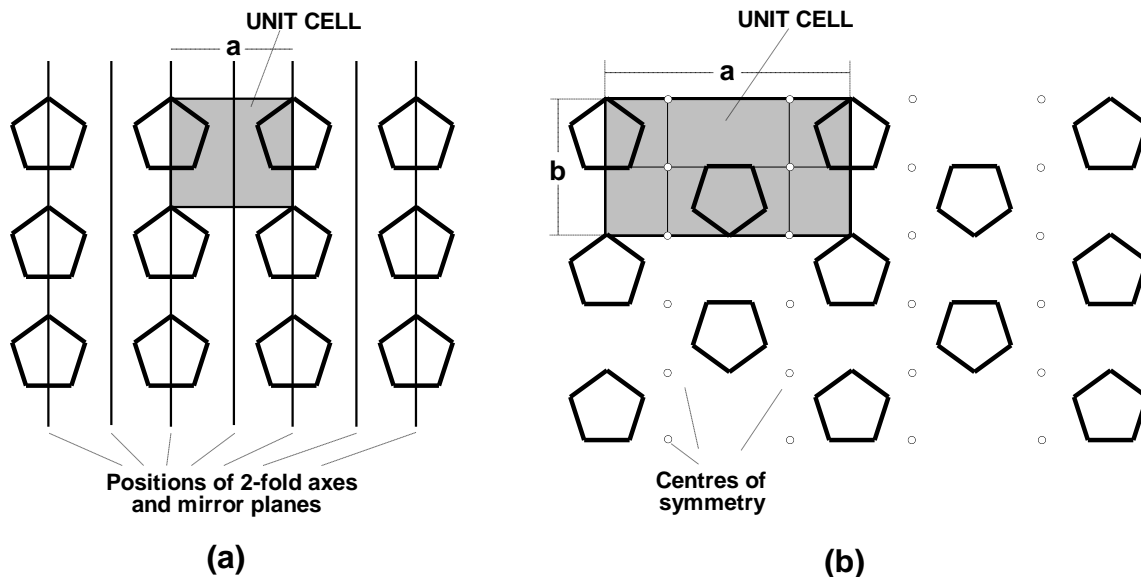


Fig. 5

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
		2
Rhombohedral	P and R	25
		25
Hexagonal	P	27
		27

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.

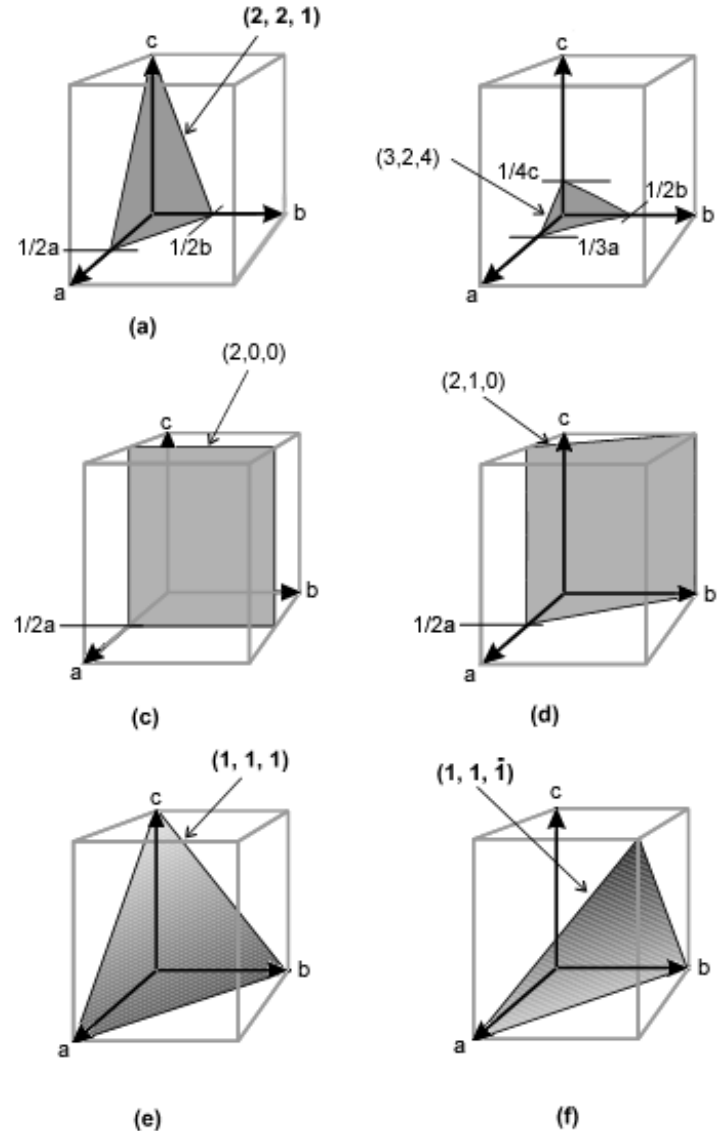
Space Group determination is an important step in crystal structure determination.

Fig. 9

CRYSTAL PLANES AND MILLER INDICES

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.

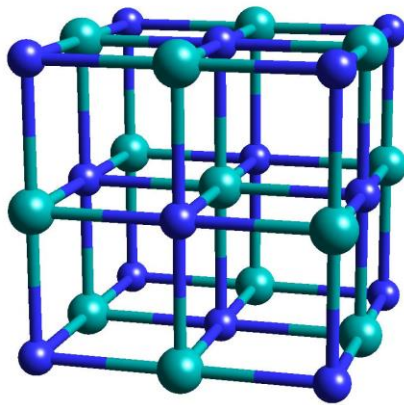
In (a) the intercepts are $\frac{1}{2}$, $\frac{1}{2}$, 1 and the Miller Indices are (2 2 1).
In (c) the intercepts on b and c are at infinity the inverse of which is 0 and the plane is the (2 0 0).
In (f) the plane cuts the negative c axis at -1 and thus is (1 1 $\bar{1}$). In crystallography -1 is often written $\bar{1}$ and pronounced "Bar 1".



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**



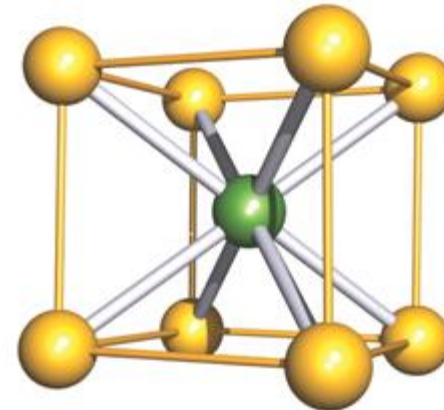
Stoichiometry (formula) from the Unit Cell

Site	Na ⁺	Cl ⁻	
Central	0	1	The unit cell of a cubic close packed metal has a face centered lattice
Face	6/2	0	
Edge	0	12/4	The formula of the unit cell is: $6 \times \frac{1}{2} + 8 \times \frac{1}{8} = 4$
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

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



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/cm³): 8.90

Volume of cell (10⁶ pm³): 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.*

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 = $n\lambda$.

The path difference is $2my$. Since $my/d = \sin\theta$
 $2my = 2d\sin\theta = n\lambda$
 where d is the interplanar spacing.

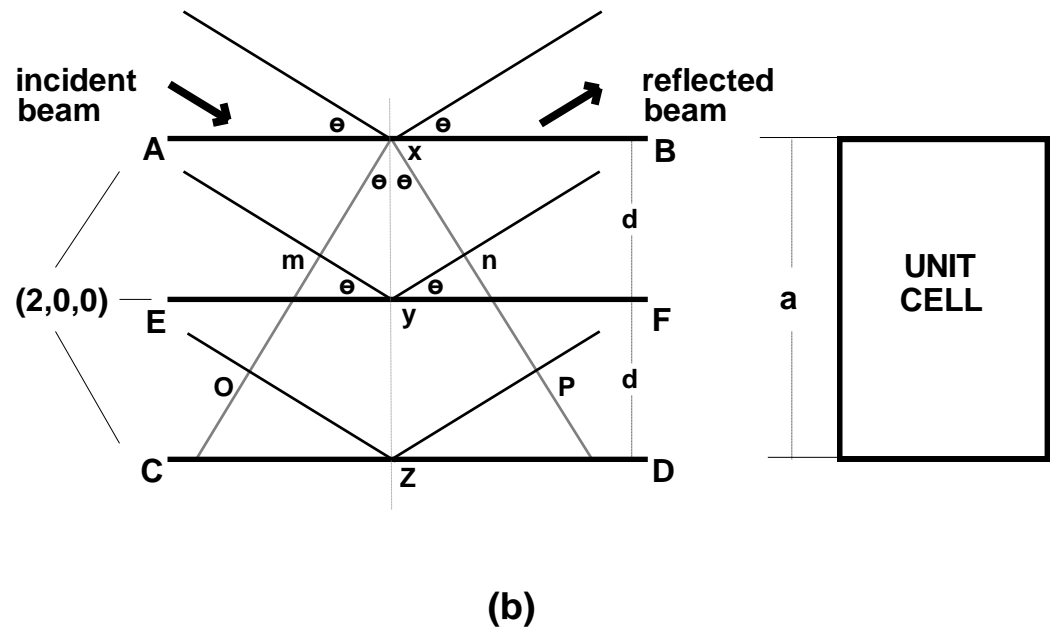
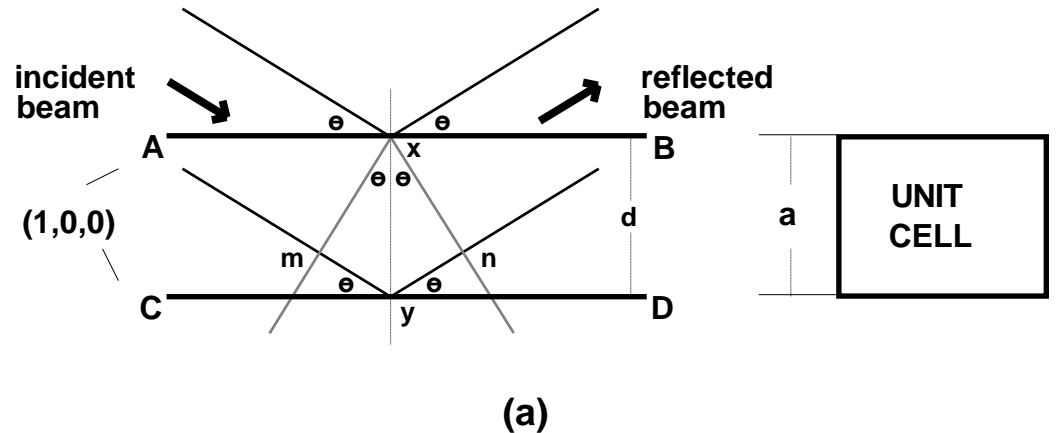


Fig. 11

Determination of the Lattice type

High symmetry can lead to reflections being systematically absent from the data set. Absent reflections have no measurable intensity.

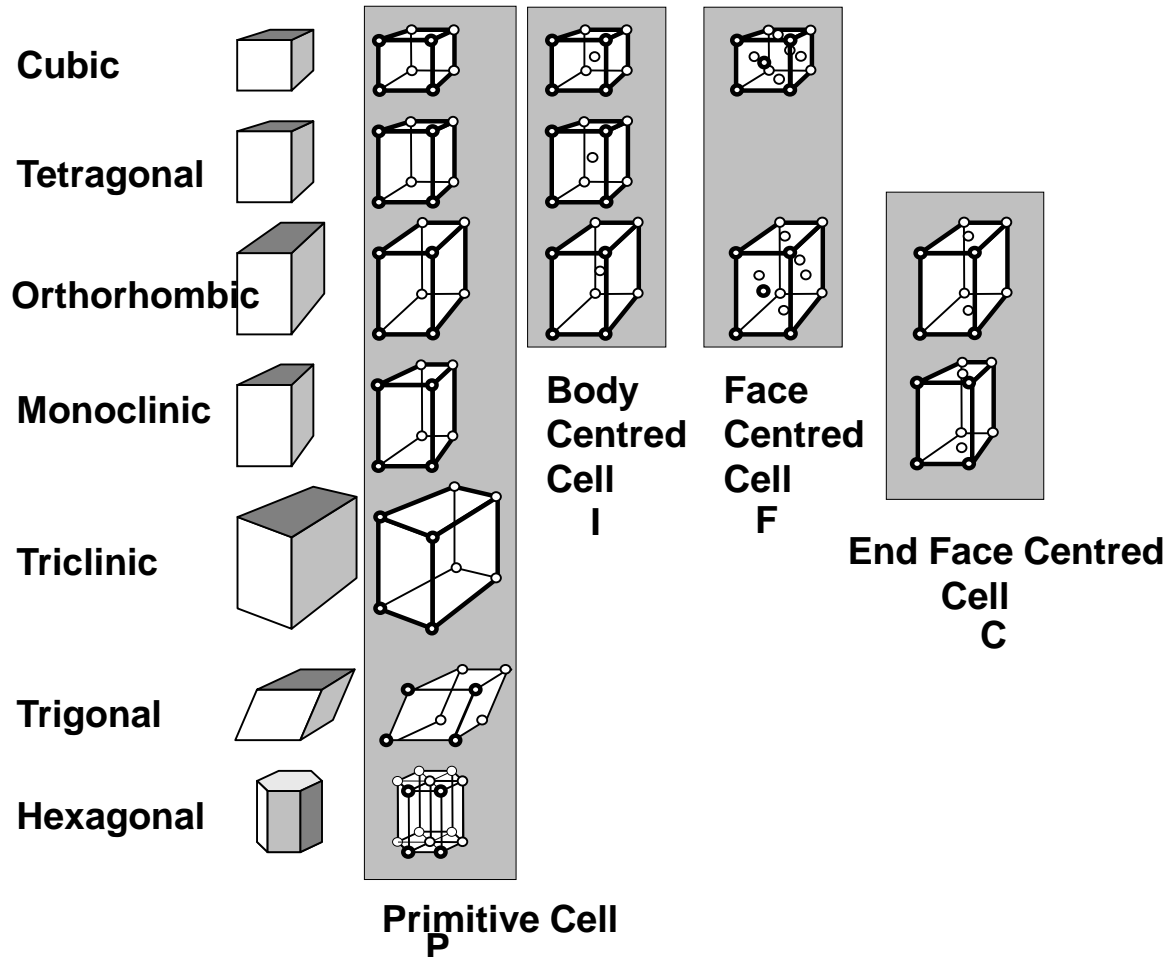
The general absences determine the lattice type;

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.



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

Determination of the Lattice parameters

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

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

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

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

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

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 λ are constant and if $\lambda^2/4a^2 = A$

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

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

Lattice Parameter Determination

Example for an FCC material

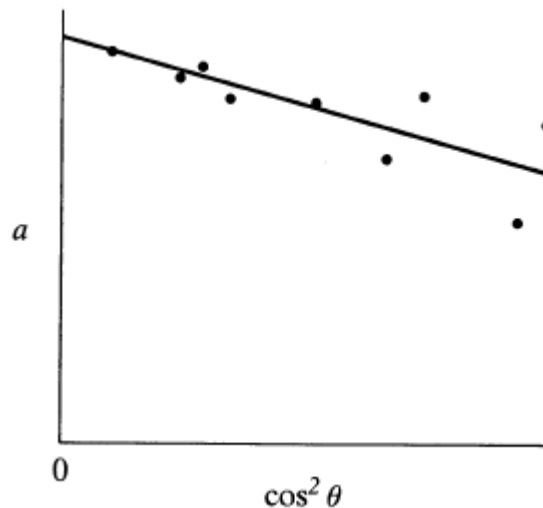
1	2	3	4	5	6	7	8	9	10
			FCC			SC		BCC	
Line	$\sin^2 \theta$	$s = (h^2 + k^2 + l^2)$	$\frac{\sin^2 \theta}{s} = \frac{\lambda^2}{4a^2}$	$a(\text{\AA})$	hkl	s	$\frac{\sin^2 \theta}{s}$	s	$\frac{\sin^2 \theta}{s}$
1	0.140	3	0.0467	3.57	111	1	0.140	2	0.0700
2	0.185	4	0.0463	3.59	200	2	0.093	4	0.0463
3	0.369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

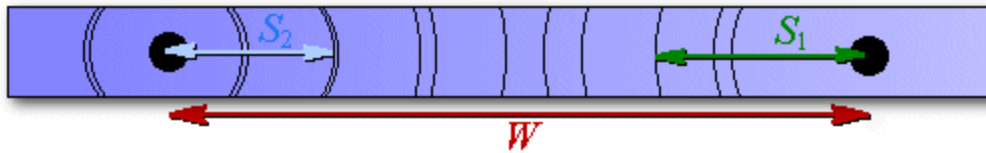
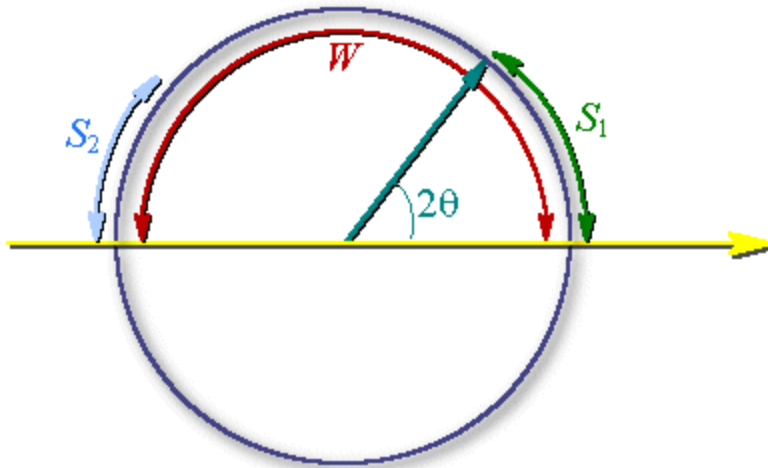
- Calculation of the lattice parameter from one peak is prone to error due to
 - Displacement of the specimen from the diffractometer axis
 - Misalignment of the instrument
 - Use of a flat specimen instead of a specimen curved to conform to the focusing circle
 - Absorption in the specimen
 - Vertical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

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

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

$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}$$

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

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
				Constant; so it is FCC	

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 g and $\lambda = 1.5405 \text{ \AA}$.

Index the diffraction data and calculate the density of aluminium.

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

Aluminum 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 θ	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 ρ (g. cm.^{-3}), the mass of the unit cell is
 $\rho \times 66.40356 \times 10^{-24} \text{ g.}$

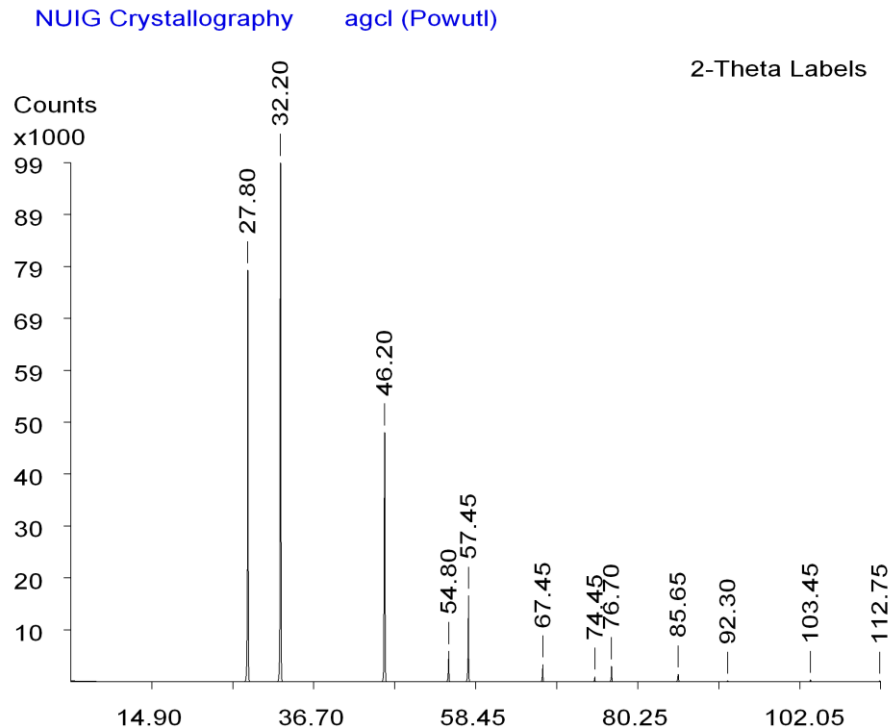
The unit cell of aluminium contains 4 atoms.

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 179.209×10^{-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\AA 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 6.022×10^{23})

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

2θ	θ	$\text{Sin}^2\theta$	Calc. $\text{Sin}^2\theta$
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 $\text{Sin}^2\theta = A(h^2 + k^2 + l^2)$ 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) 2θ

$a^2 = 30.7692$

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

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 $573.284 / (6.02 \times 10^{23})$

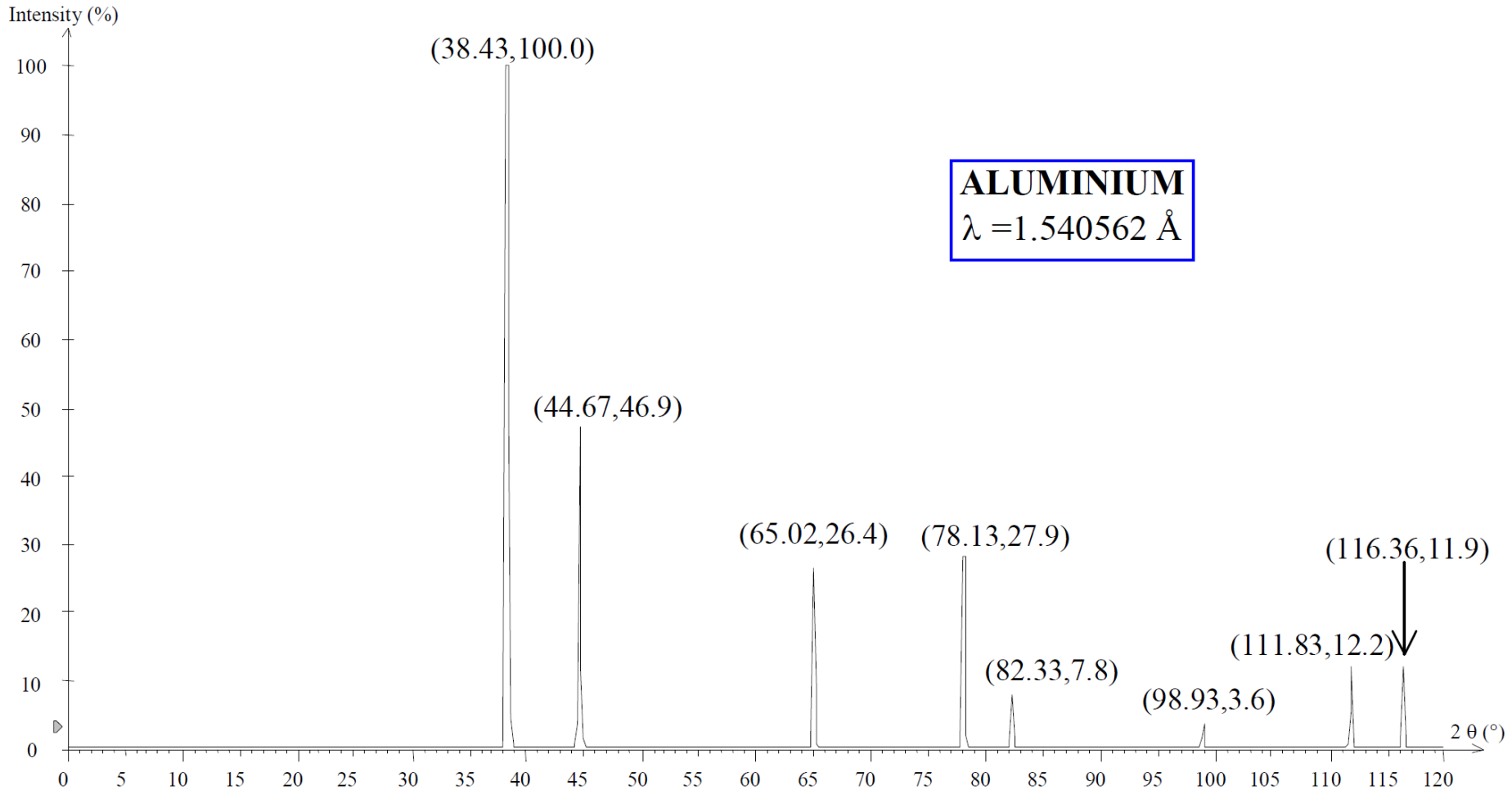
Density = $573.284 / (6.02 \times 10^{23})(5.547 \times 10^{-8})^3$

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

Density = 5.580 g/cm^3

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 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	$\sin^2 \theta$	$1 \times \frac{\sin^2 \theta}{\sin^2 \theta_{\min}}$	$2 \times \frac{\sin^2 \theta}{\sin^2 \theta_{\min}}$	$3 \times \frac{\sin^2 \theta}{\sin^2 \theta_{\min}}$	$h^2 + k^2 + l^2$	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							

X-RAY FLUORESCENCE (XRF)

X-ray fluorescence 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)

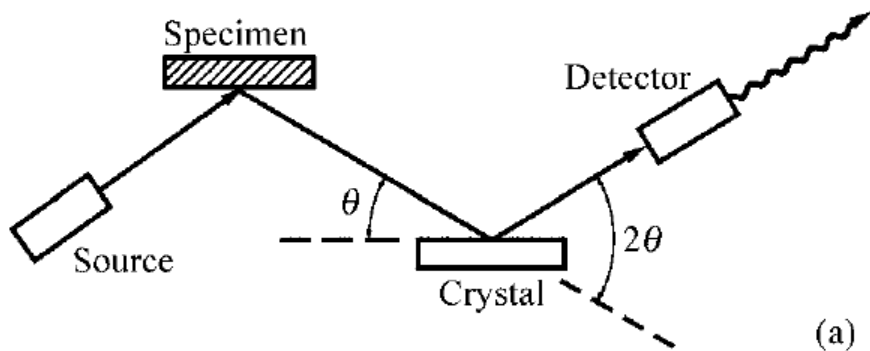
Energy dispersive spectroscopy (EDS)

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

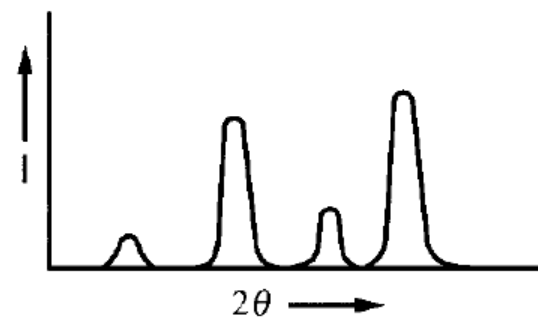
Measurement time varies between seconds and about 30 minutes per sample depending on the number of determined elements

The quantitative analysis based on measurement results takes seconds to complete

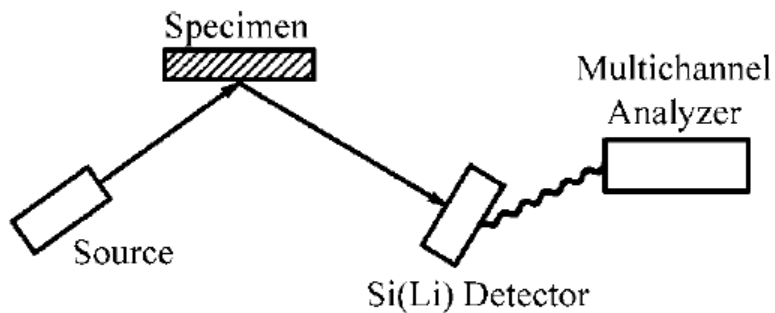
**WDS
(WDXRF)**



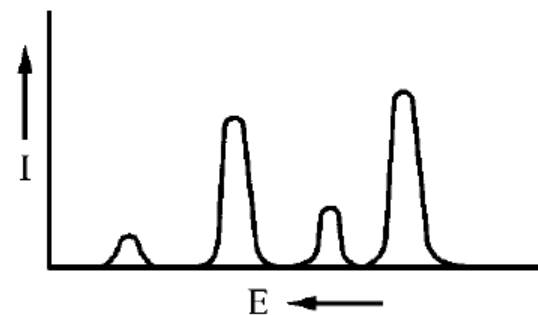
(a)



**EDS
(EDXRF)**



(b)



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

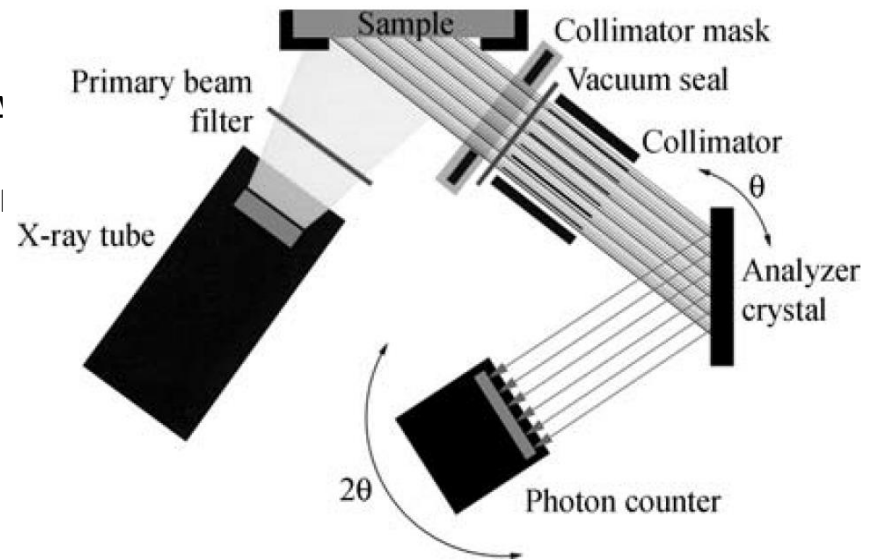
WDS (Wavelength Dispersive Spectroscopy)

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 Å 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

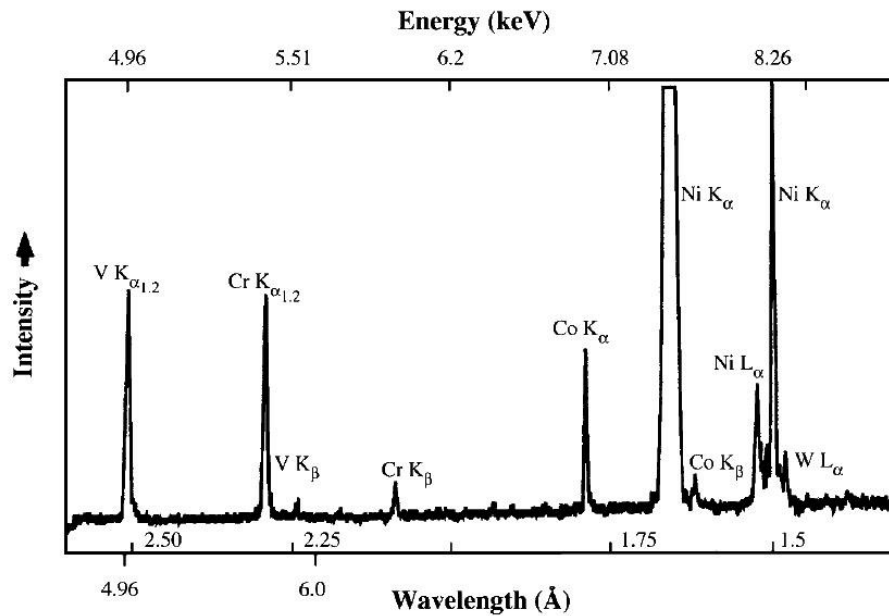
Bragg law is used to calculate the wavelength range that are detectable by a crystal

A maximum θ degree of 73 is applicable

Crystal	Plane	Plane spacing, $2d$ (Å)	Atomic number range	
			<i>K</i> lines	<i>L</i> lines
Lithium fluoride (LiF)	(220)	2.848	> Ti(22)	> La(57)
Lithium fluoride (LiF)	(200)	4.028	> K(19)	> Cd(48)
Pentaerythritol (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)	–

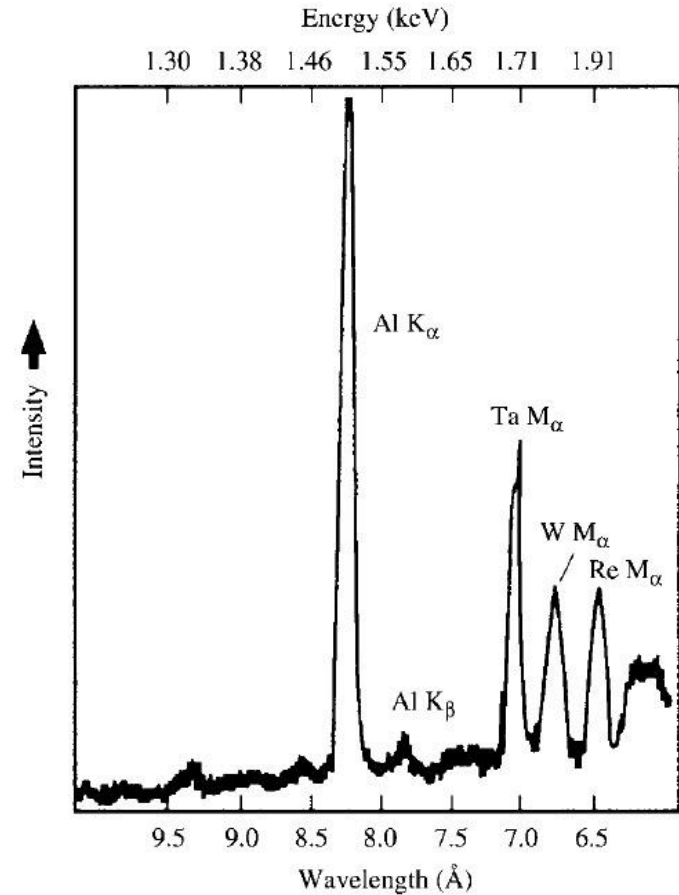
WDS

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

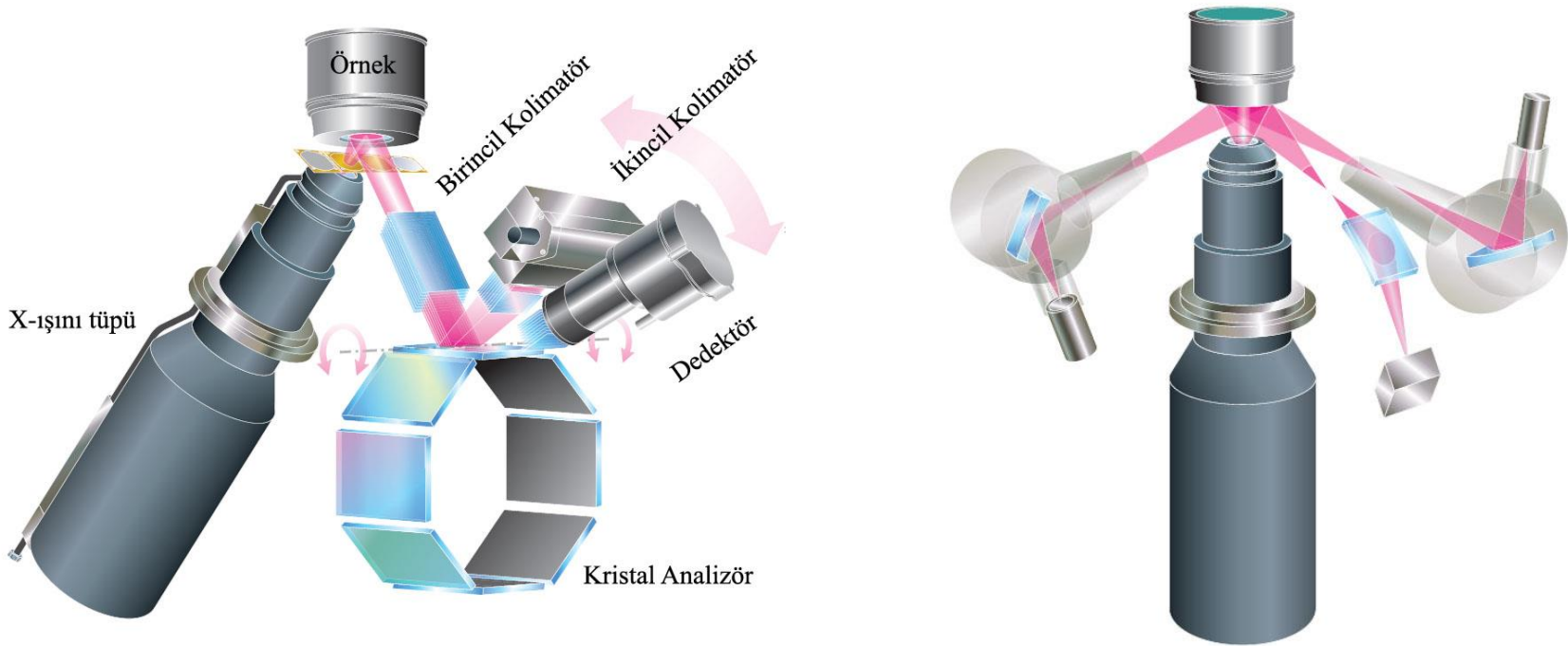


WDS

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

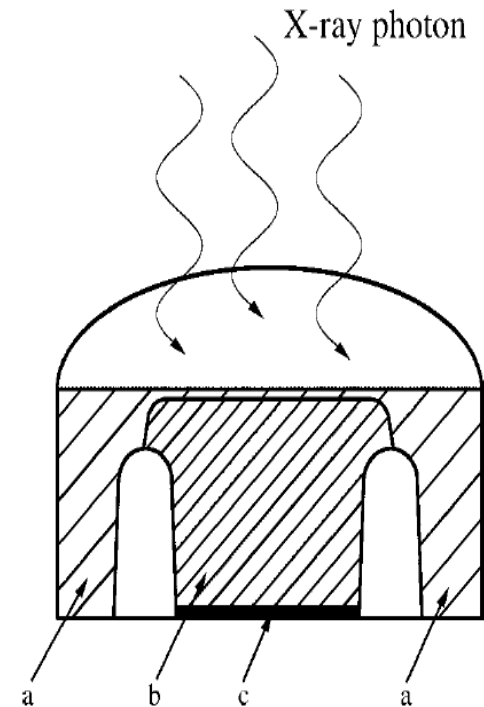
Si(Li) detector is used in a typical EDS system. This detector is composed of a small cylinder of p-type Si and Li, combined in the form of a diode.

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

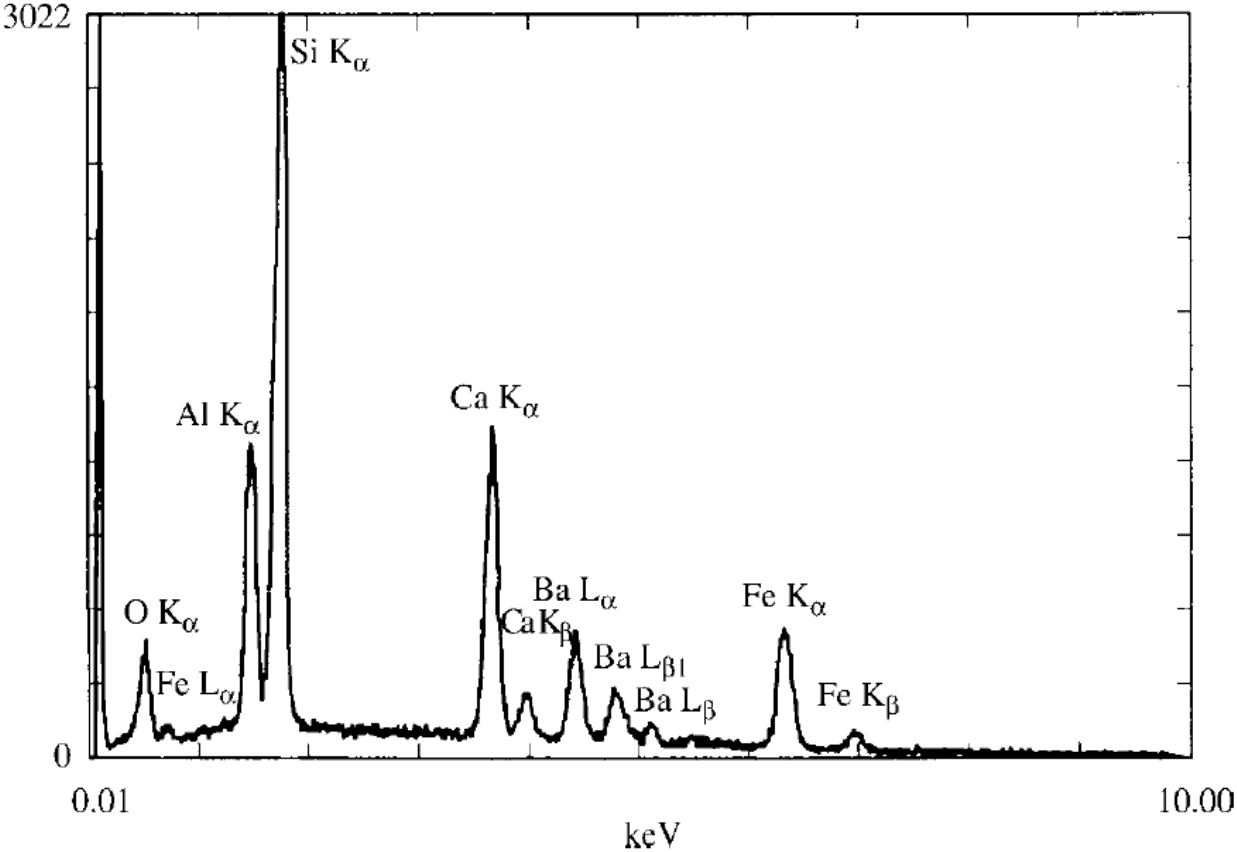


A: P-tipi silisyum

B: lityum bölgesi

C: n-tipi silisyum

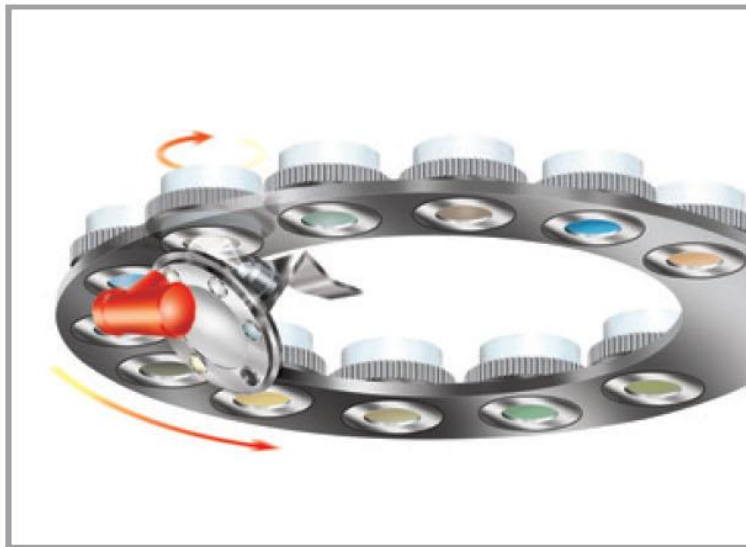
EDS Spectrum



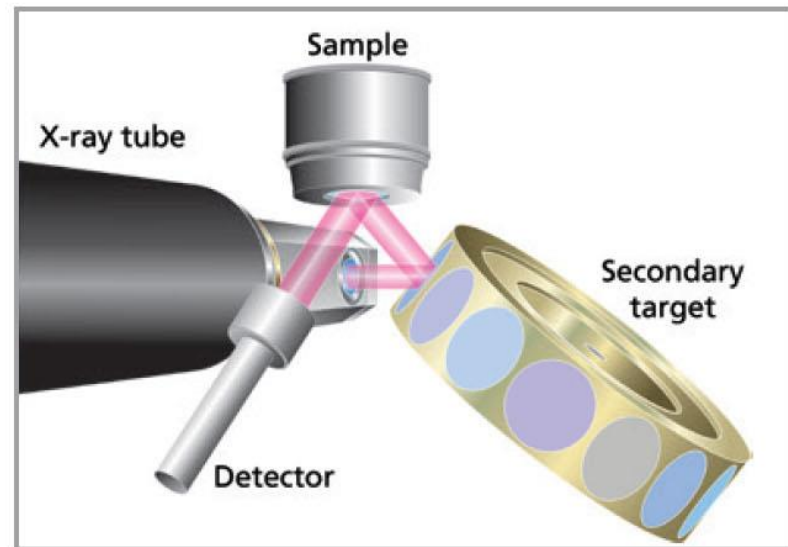
EDS analysis of glass

EDXRF Geometry

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



2D optik sistemli



3D optik sistemli

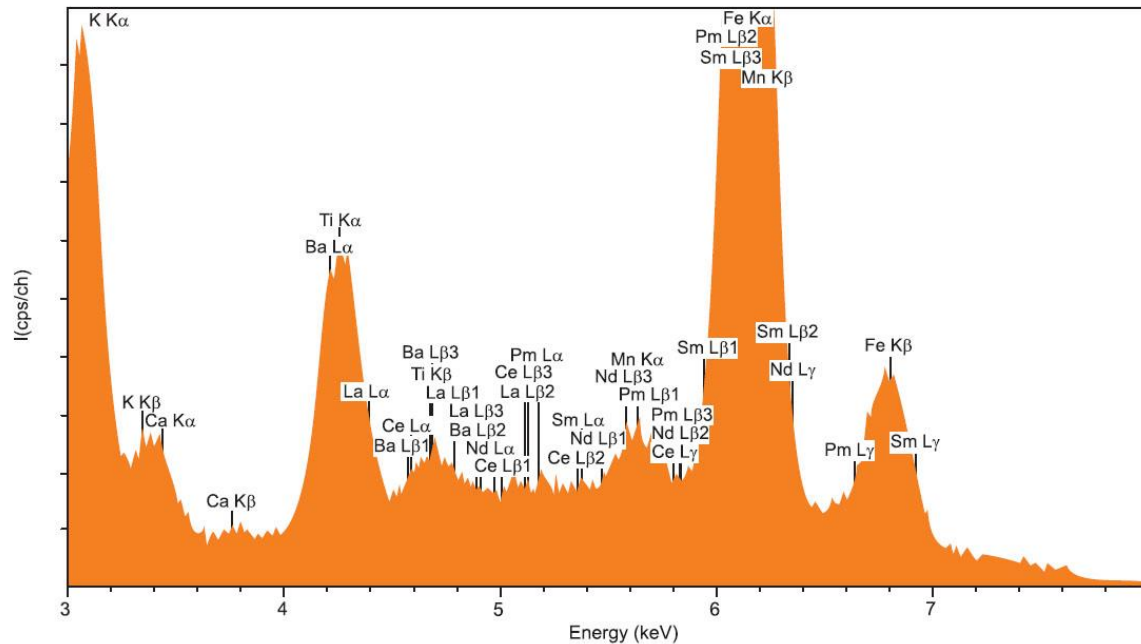
EDS(EDXRF) spectroscope with 2D optical system

- 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



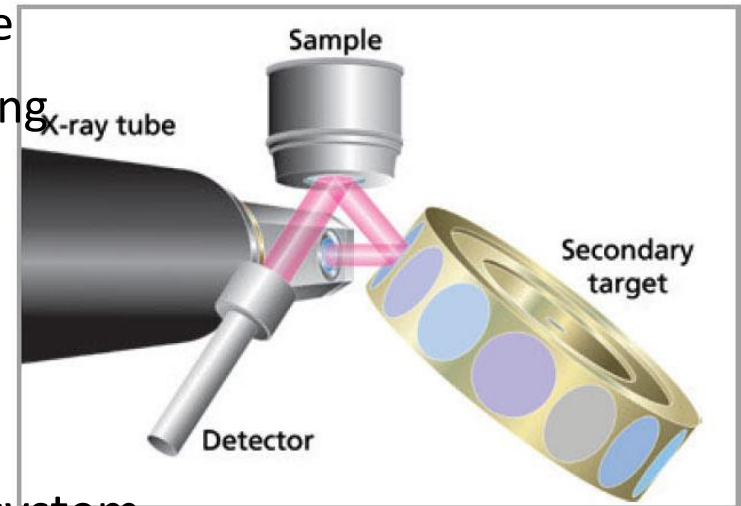
EDS(EDXRF) spectroscopy with 2D optical system



EDXRF spectrum of soil

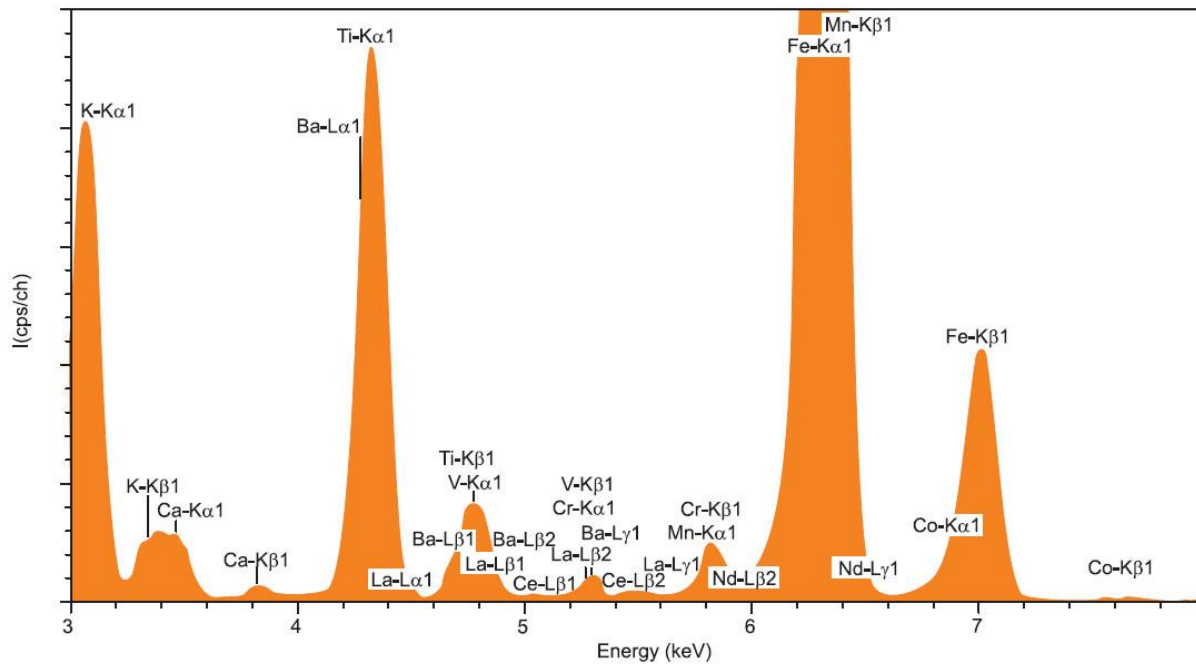
EDS(EDXRF) spectroscopy with 3D optical system

- 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



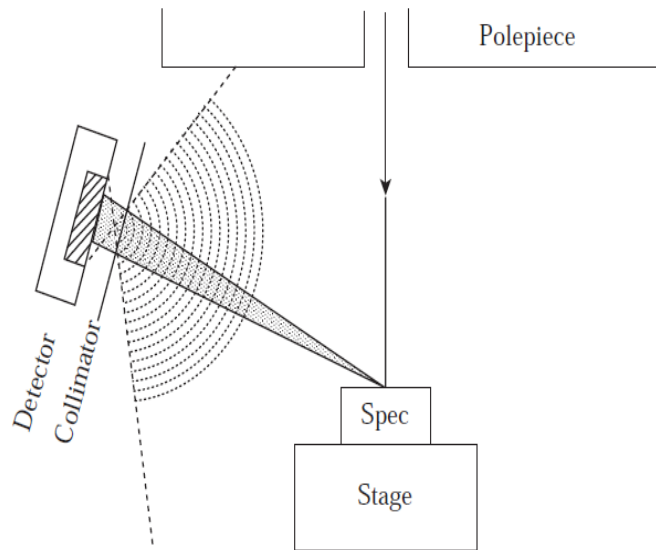
EDXRF spectrum of soil using 3D optical system

EDS detector in the SEM

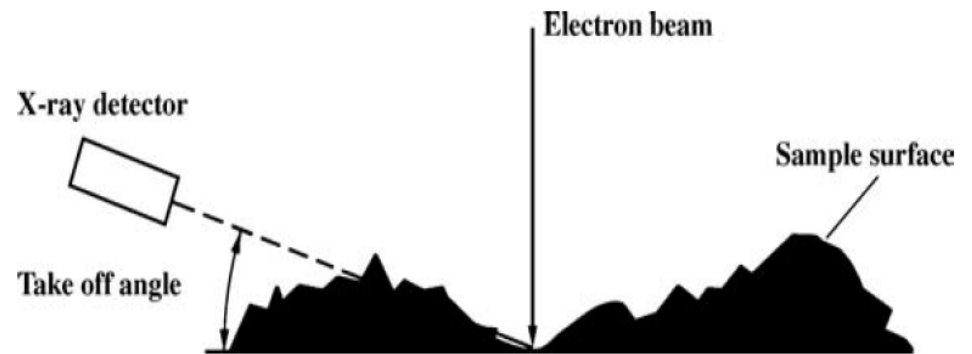
- EDS detectors are integrated into the SEM and TEM because they are simpler than WDS. This setup enables elemental analysis during microstructural analysis.

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

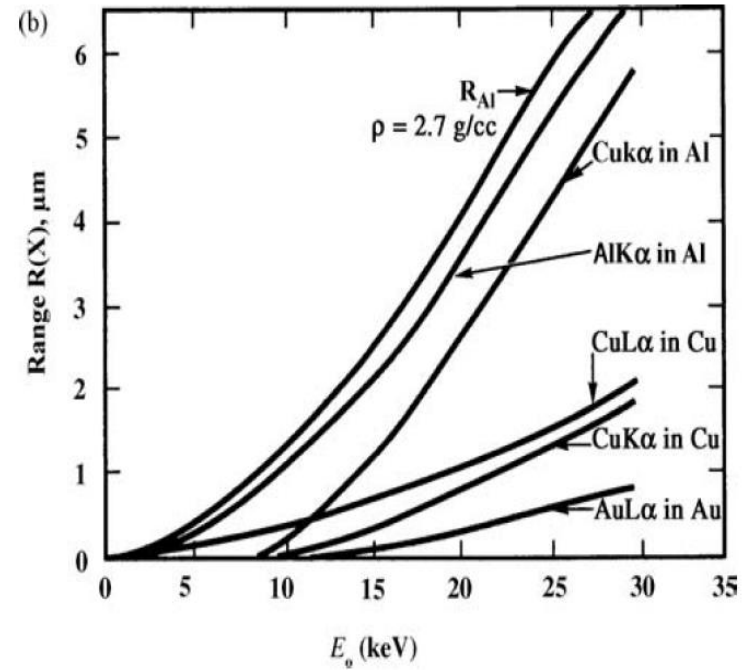
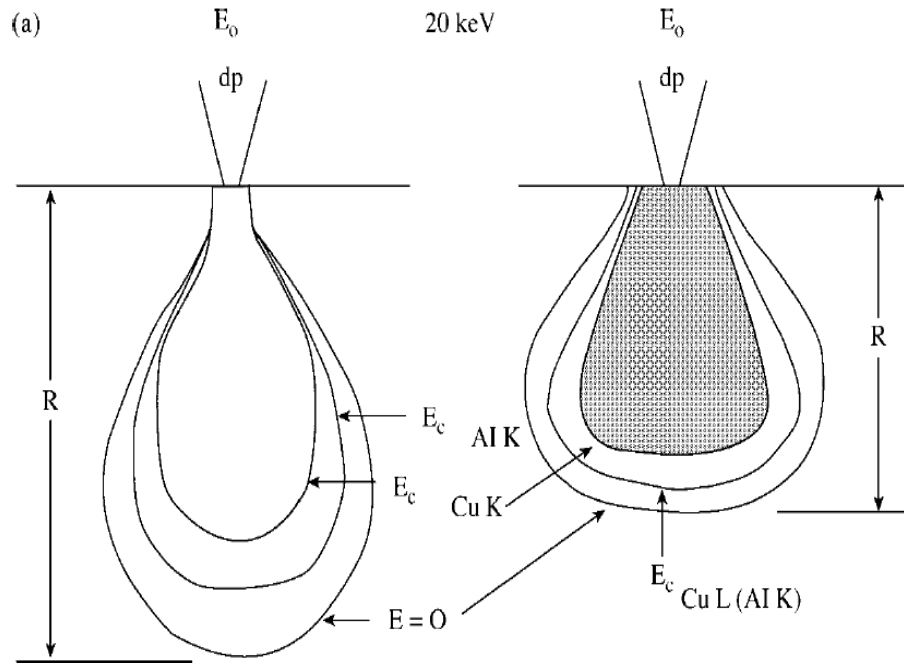


EDS setup in a TEM



Orientation of the X-ray detector for rough surface analysis

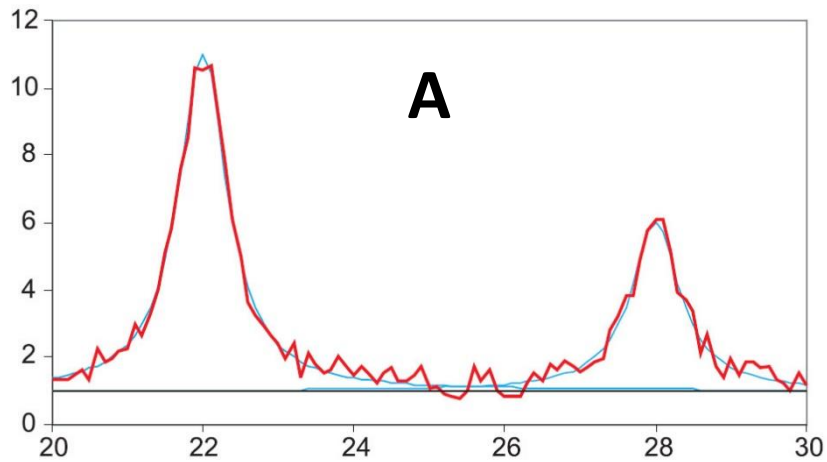
X-ray fluorescence zones from samples with different atomic numbers



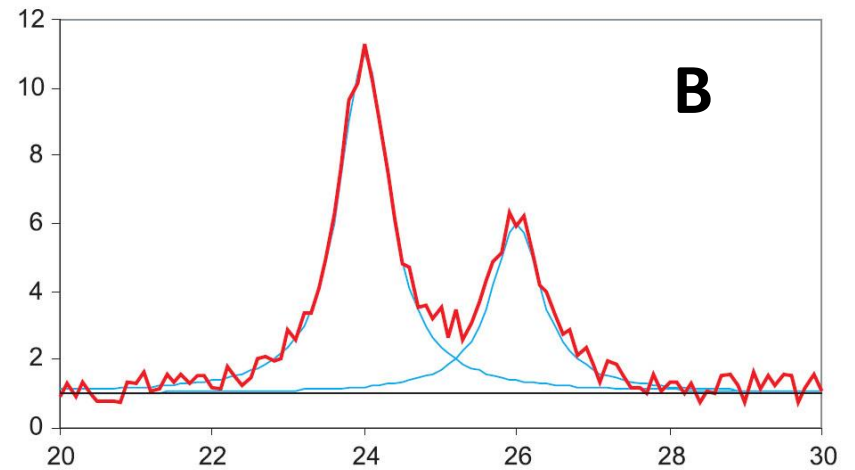
Comparison of WDXRF and EDXRF Techniques

	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

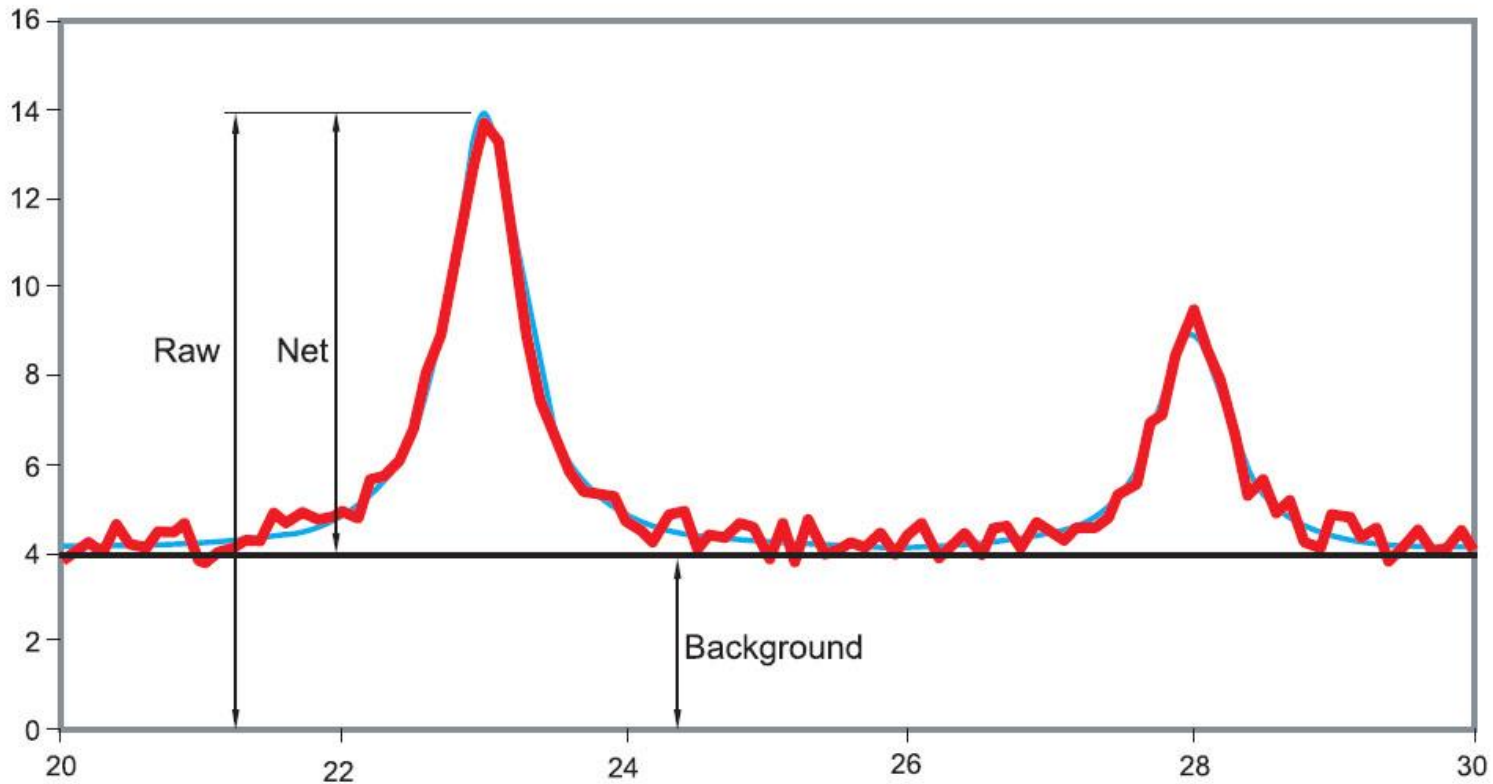
Background and profile corrections



Background correction for two separate peaks

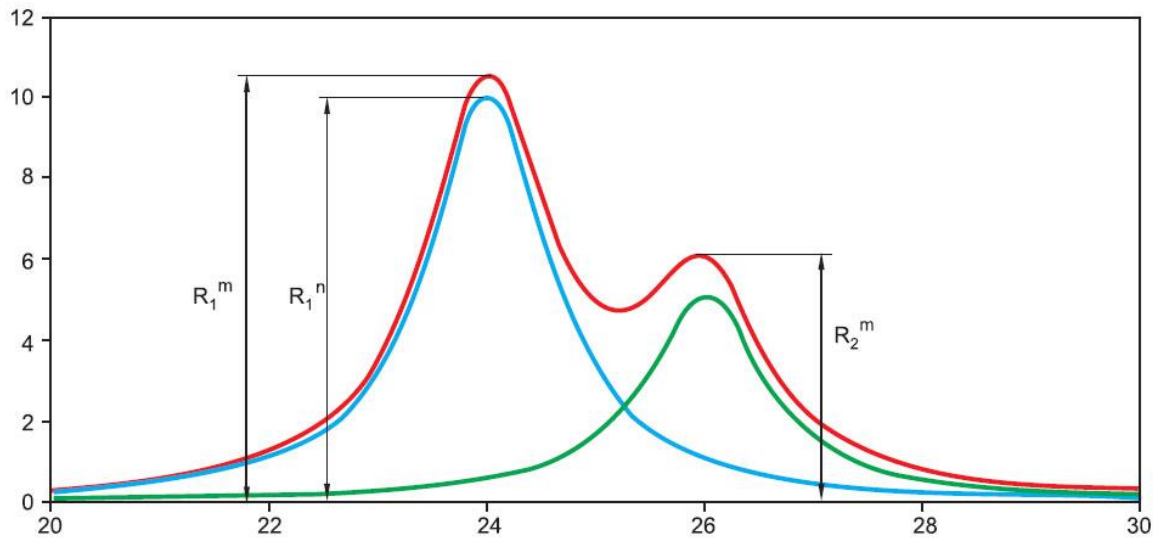


Background correction and peak profiling for two overlapping peaks



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

$$X = M * K * I_R$$

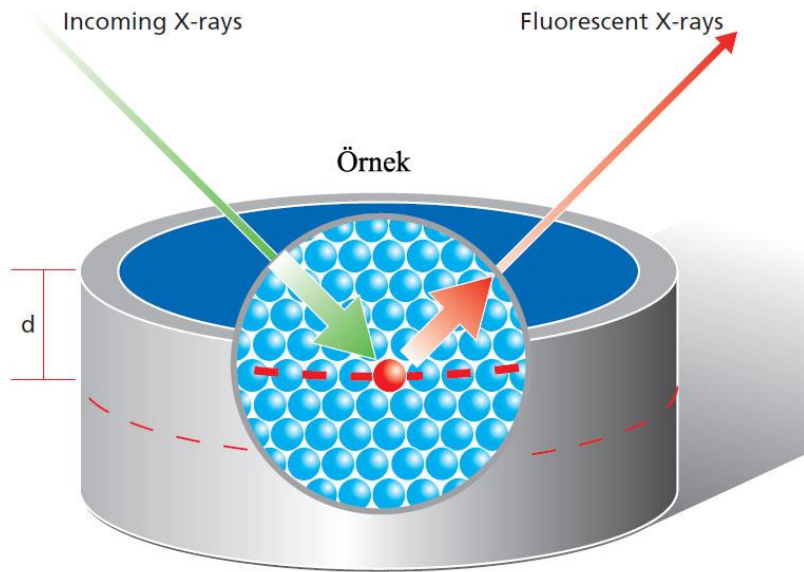
Weight fraction of an element (X) is proportional to its relative intensity (I_R) by the instrument factor (K) and the sample matrix factor (M).

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

M contains 3 basic matrix factors:

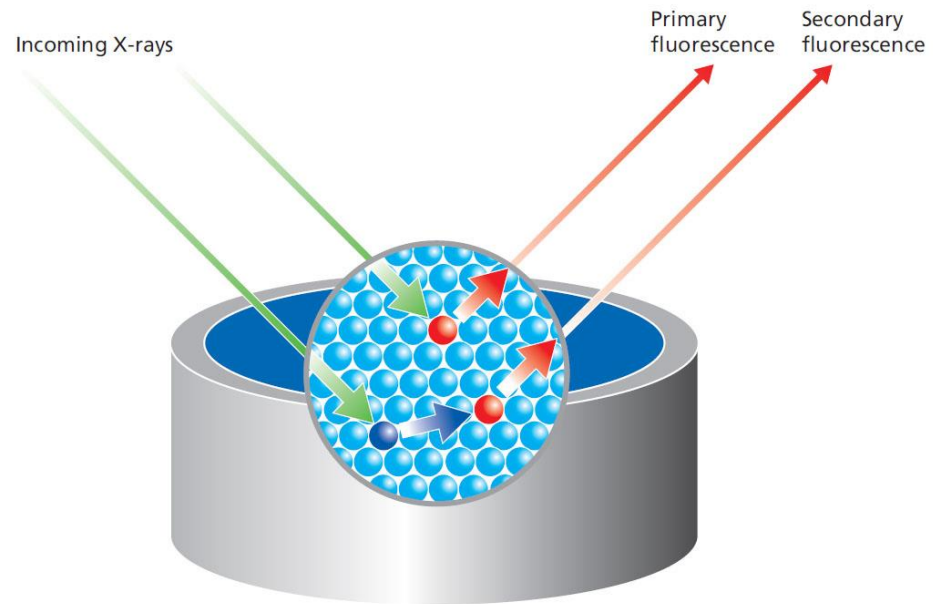
1. Absorption of the X-ray by the sample
2. Secondary absorption
3. Secondary fluorescence

A



Absorption by the sample

B



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