CHEMISTRY

74th Class, 15-12-2021

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Last class

- Characterisation, techniques
- X-ray diffraction

In this class

- Characterisation, techniques
- X-ray diffraction, continuation

CLA3 – Practical component

- **Model Practical Examination/CLA3 [Starts from 17/12/2021/V day order/ Friday]**
- **22-12-2021, Wednesday, III day order, 1.25 – 2.10 pm**
- QP pattern: 25 MCQs [Through GCR]
- Maximum marks:25
- Duration: 45 min

Spectroscopy

Spectroscopy: Spectroscopy is the study of the interaction between matter and electromagnetic radiation. Electromagnetic radiation, is composed of electrical and magnetic waves which oscillate on perpendicular planes

- ❑ It is based on ***the analysis of EM radiation that is emitted, absorbed, or scattered by molecules***, which can give information on:
- ➢ Chemical analysis (finding a chemical fingerprint, so to speak)
- ➢ molecular structure (bond lengths, angles, strengths, energy levels, etc...)

Light: Electromagnetic radiation

Electromagnetic radiation

- ❑ Also known as radiant heat or radiant energy
- ❑ One of the ways by which energy travels through space
- ❑ Consists of perpendicular electric and magnetic fields that are also perpendicular to direction of propagation

Examples
heat energy in microwaves
light from the sun
X-ray
radio waves

Regions of the spectra

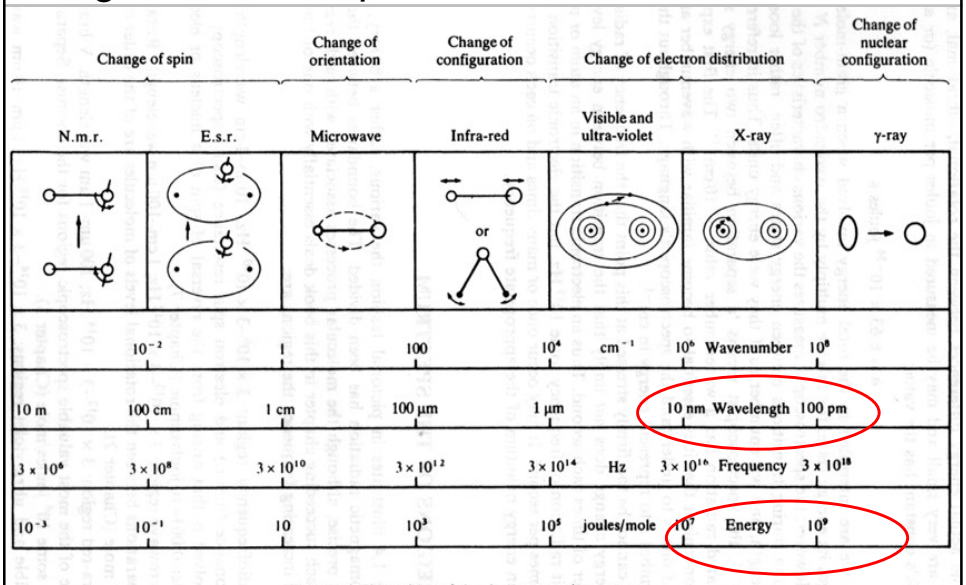
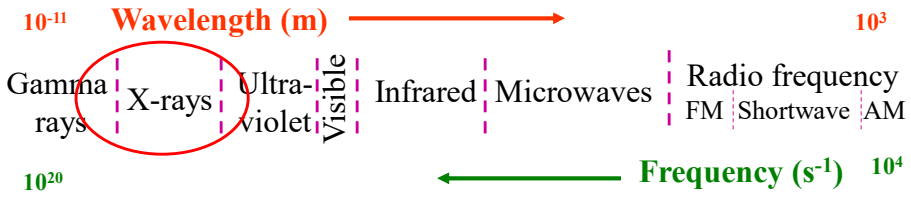


Figure 1.4 The regions of the electromagnetic spectrum.

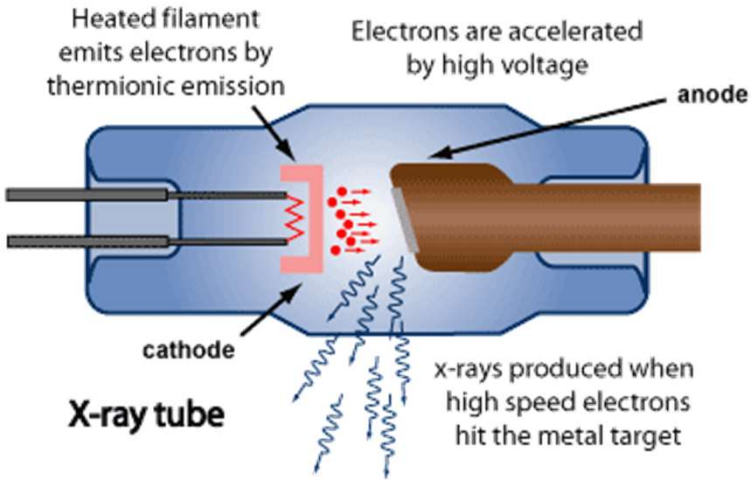
Electromagnetic spectrum



- X-rays, a form of electromagnetic radiation
- Most X-rays have a wavelength ranging from **0.01 to 10 nanometers**, corresponding to frequencies in the range **30 petahertz to 30 exahertz** (3×10^{16} Hz to 3×10^{19} Hz) and energies in the range **100 eV to 100 keV**

X–ray, 1895

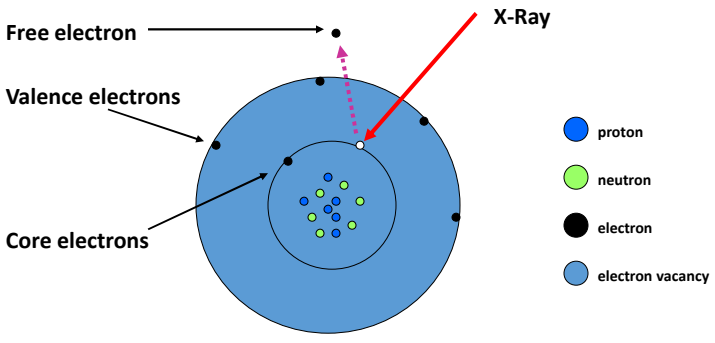
X-rays



What is XPS?

- X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA) is a widely used technique to investigate the chemical composition of surfaces.
- X-ray Photoelectron Spectroscopy (XPS) uses **soft X-rays (with a photon energy of 200-2000 eV) to examine electrons in core-levels**.
- Surface technique

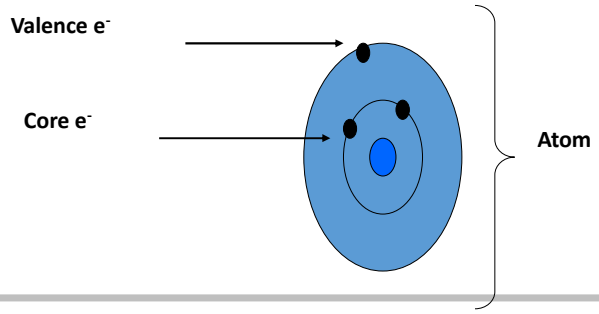
The atom and the X-Ray



The core electrons respond very well to the X-Ray energy

Why the core electrons?

- The **core e$^-$s have a higher probability of matching the energies of AlKα and MgKα**
- The core e$^-$s are close to the nucleus and have **binding energies characteristic of their particular element**
- An electron near the Fermi level is far from the nucleus, moving in different directions all over the place, and will not carry information about any single atom.



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X-rays

- The X-Ray source produces photons with certain energies:
  - MgKα photon with an energy of **1253.6 eV**
  - AlKα photon with an energy of **1486.6 eV**
- Normally, the sample will be radiated with photons of a single energy (MgKα or AlKα). This is known as a monoenergetic X-ray beam
- Irradiate the sample surface, **hitting the core electrons** (e^-) of the atoms
- The X-rays penetrate the sample to a **depth on the order of a micrometer**
- Useful e^- signal is obtained **only from a depth of around 10 to 100 Å** on the surface

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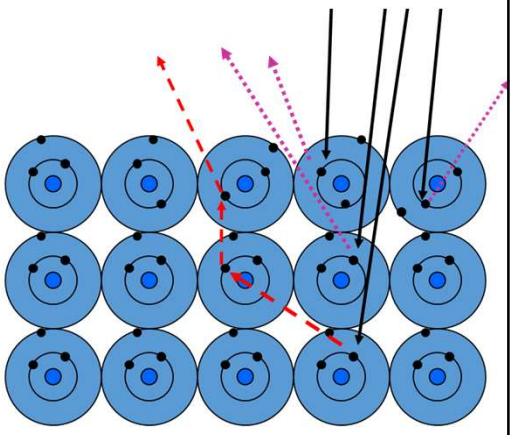
X-rays on the surface

- The X-rays will penetrate to the core e^- of the atoms in the sample
- Some e^-s are going to be released without any problem giving the **Kinetic Energies (KE) characteristic of their elements**
- Other e^-s will come from inner layers and collide with other e^-s of upper layers
  - These e- will be in **lower energy**
  - They will contribute to the **noise signal** of the spectrum



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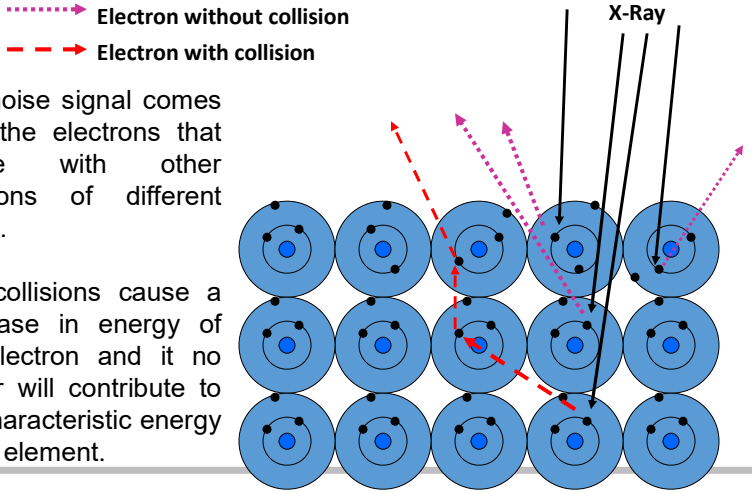

- The noise signal comes from the electrons that collide with other electrons of different layers.
- The collisions cause a decrease in energy of the electron and it no longer will contribute to the characteristic energy of the element.

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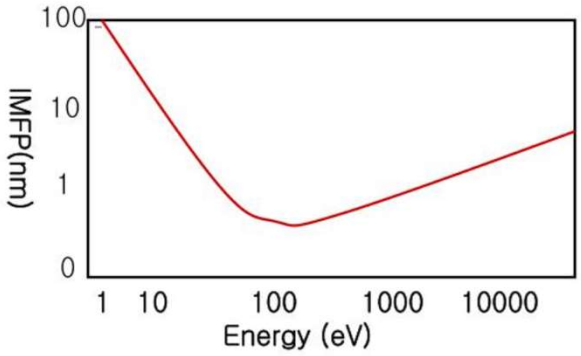
Inelastic mean free path



The inelastic mean free path (IMFP) of electrons is *less than 1 nm* for electron energies with 10~1000 eV.

The inelastic mean free path (IMFP) is an index of how far an electron on average travels through a solid before losing energy.

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XPS background

- XPS technique is based on Einstein's idea about the photoelectric effect, developed around 1905
  - The concept of photons was used to describe the ejection of electrons from a surface when photons were impinged upon it
- During the mid 1960's **Dr. Kai Siegbahn** and his research group developed the XPS technique. (Uppsala university)
  - In **1981, Dr. Siegbahn was awarded the Nobel Prize** in Physics for the development of the XPS technique

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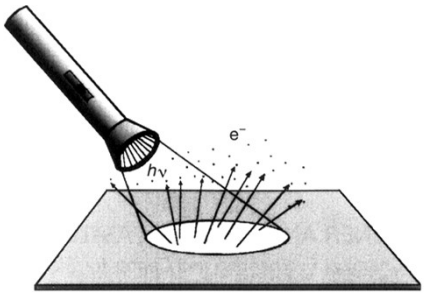
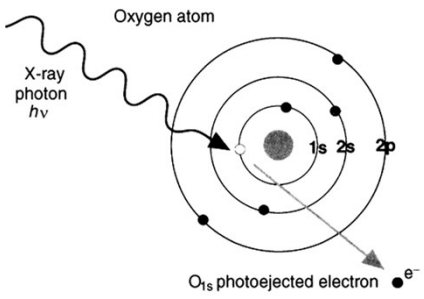
Photoelectric effect

Einstein, Nobel Prize 1921





Photoemission as an analytical tool

Kai Siegbahn, Nobel Prize 1981

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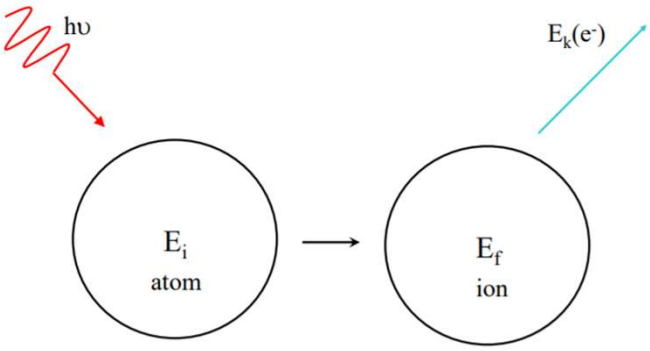
The Photoelectric process



$$h\upsilon + E_i = E_k(e^-) + E_f$$

$$h\upsilon - E_k(e^-) = E_f - E_i = E_b$$

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The Photoelectric process

$$A + h\nu = A^+ + e^-$$

1. Conservation of energy then requires that :

$$E(A) + h\nu = E(A^+) + E(e^-) \quad \text{(energy is conserved)}$$

2. Since the energy of the electron is present solely as kinetic energy (KE) this can be rearranged to give the following expression for the KE of the photoelectron :

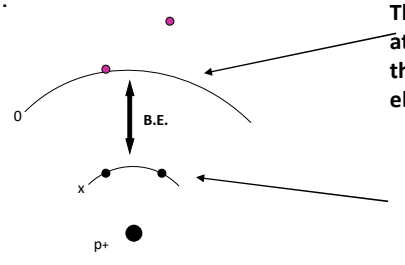
$$E(e^-) = KE(e^-) = h\nu - [E(A^+) - E(A)]$$

3. The final term in brackets represents the difference in energy between the ionized and neutral atoms, and is generally called the *binding energy* (BE) of the electron - this then leads to the following commonly quoted equation :

KE = hν - BE

Binding Energy (BE)

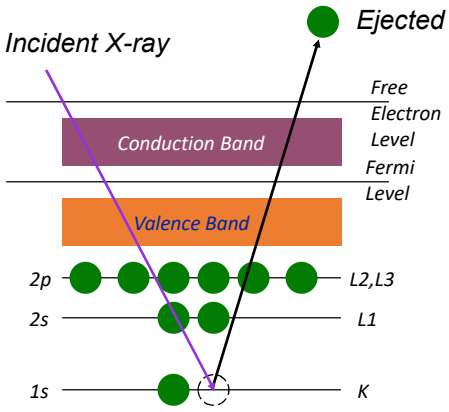
- The Binding Energy (BE) is characteristic of the core electrons for each element.
- The BE is determined by the **attraction of the electrons to the nucleus**. If an electron with energy **x is pulled away from the nucleus, the attraction between the electron and the nucleus decreases and the BE decreases**.
- Eventually, there will be a point when the electron will be free of the nucleus.



This is the point with 0 energy of attraction between the electron and the nucleus. At this point the electron is free from the atom.

These electrons are attracted to the proton with certain binding energy x

The photoelectric process



- *XPS spectral lines are identified by the shell from which the electron was ejected (1s, 2s, 2p, etc.).*
- *The ejected photoelectron has kinetic energy:*
- ***KE = hv-BE***

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Equation

$$KE = h\nu - BE - \emptyset$$

KE ⟶ Kinetic Energy (measured in the XPS spectrometer)

hv ⟶ photon energy from the X-Ray source (controlled)

Ø ⟶ The work function is a correction factor for the instrument and correlates to the minimum energy required to eject an electron from an atom. Found by calibration

BE ⟶ is the unknown variable

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How & what information is obtained ?

- The sample is **illuminated with X-rays** - monochromatic or unfiltered Al Kα or Mg Kα - and photoelectrons are emitted from the surface
- The **kinetic energy of these emitted electrons is characteristic of the element** from which the photoelectron originated
- The chemical state of an atom alters the **binding energy (BE) of a photoelectron which results in a change in the measured kinetic energy (KE)**
- The BE is related to the measured photoelectron KE by the simple equation; **BE = hv - KE** where hv is the photon (X-ray) energy

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How information is obtained ?

- The **position and intensity of the peaks** in an energy spectrum provide the desired chemical state and **quantitative information**
- The **chemical or bonding information of the element** is derived from these chemical shifts
- X-ray photoelectron spectroscopy (XPS), also known as ESCA (electron spectroscopy for chemical analysis) is a surface analysis technique which **provides both elemental and chemical state information** virtually without restriction on the type of material which can be analysed

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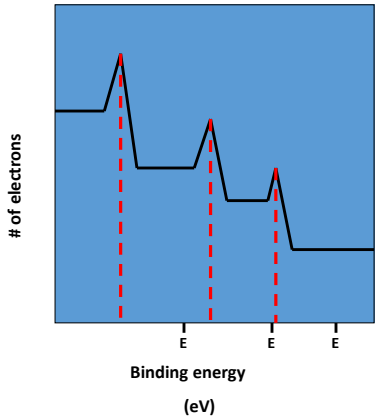
KE versus BE



- KE can be plotted depending on BE
- Each peak represents the amount of e$^-$s at a certain energy that is characteristic of some element

BE increase from right to left

1000 eV ← → 0 eV

KE increase from left to right

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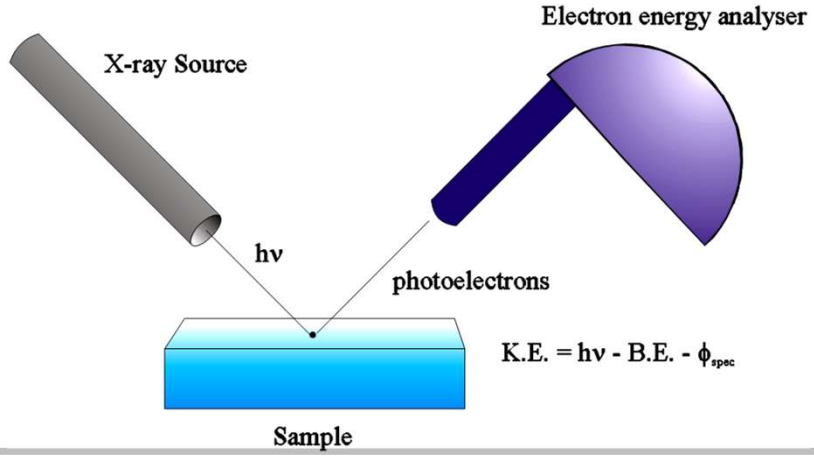
How does XPS technology work?

XPS is a widely used surface analysis technique because of its relative simplicity in use and data interpretation



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Why Does XPS Need UHV?

XPS is a surface sensitive technique

XPS measurements are conducted under ultra-high vacuum (< 10^{-9} Torr) in **order to avoid collision between photoelectrons and gas molecules in the spectrometer**, and **minimize surface contamination** from residual gases. Contaminates will produce an XPS signal and lead to incorrect analysis of the surface of composition.

- Removing contamination
  - To remove the contamination the sample surface is bombarded with argon ions (Ar^+ = 3KeV).
  - Heat and oxygen can be used to remove hydrocarbons
- The XPS technique could cause damage to the surface, but it is negligible

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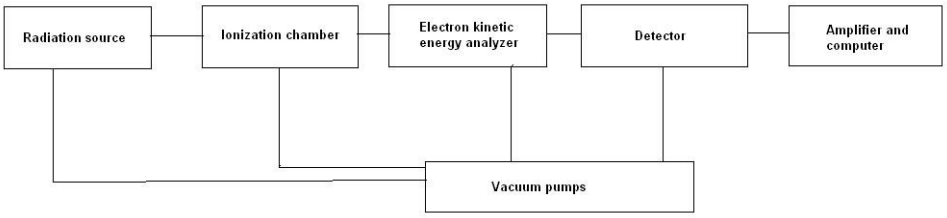
X-ray Photoelectron Spectrometer



- All photoelectron spectrometers must have three components
- The first and second are **excitation source** used to irradiate the sample into releasing electrons and **ionization chamber** respectively
- The third is an **electron energy analyzer** which will disperse the emitted photoelectrons according to their respective kinetic energy
- In addition, the spectrometer needs to **have a high vacuum environment,** which will prevent the electrons from being scattered by gas particles.

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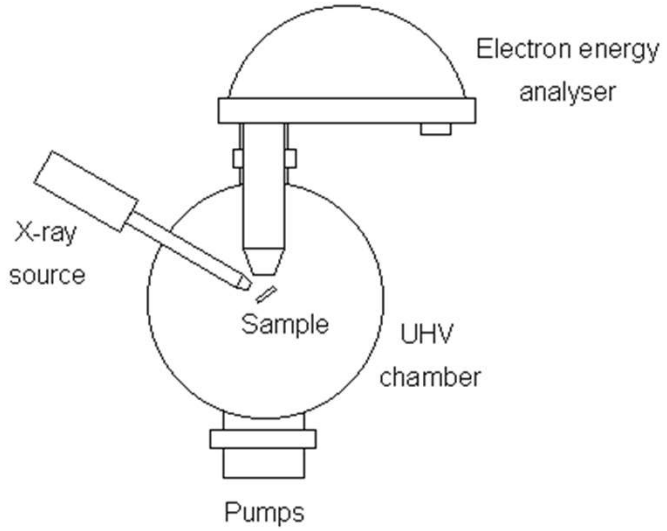
X-ray Photoelectron Spectrometer



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How does XPS technology work?

- A monoenergetic X-ray beam emits photoelectrons from the surface of the sample
- The X-Rays either of two energies:
  - Al Kα (1486.6eV)
  - Mg Kα (1253.6 eV)
- The X-ray photons - about a micrometer of the sample
- The XPS spectrum contains information only about the top 10 - 100 Å of the sample
- Ultrahigh vacuum environment to eliminate excessive surface contamination
- Cylindrical Mirror Analyzer (CMA) measures the KE of emitted e^-s
- The spectrum plotted by the computer from the analyzer signal
- The binding energies can be determined from the peak positions and the elements present in the sample identified

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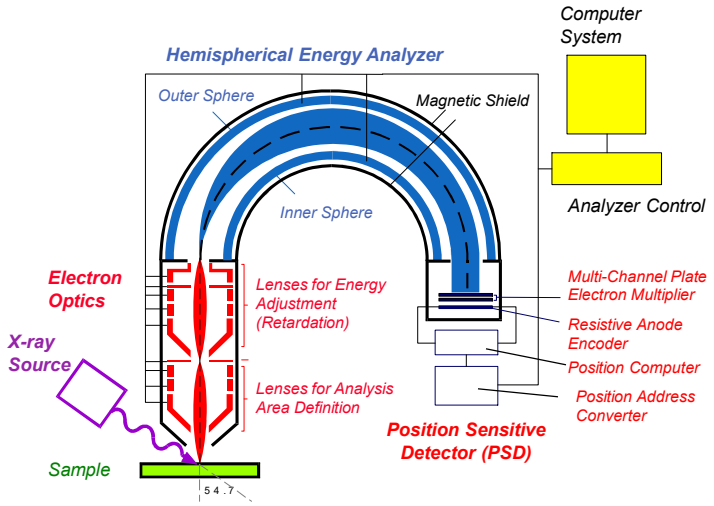
X-ray Photoelectron Spectrometer



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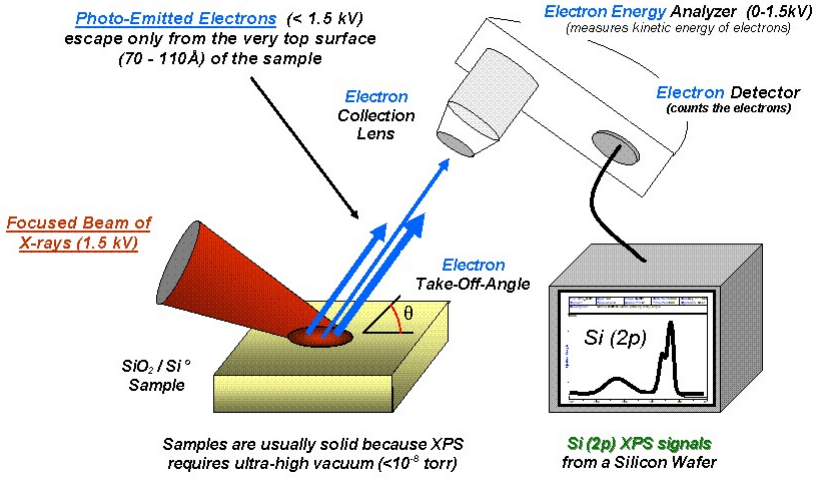
X-ray Photoelectron Spectrometer



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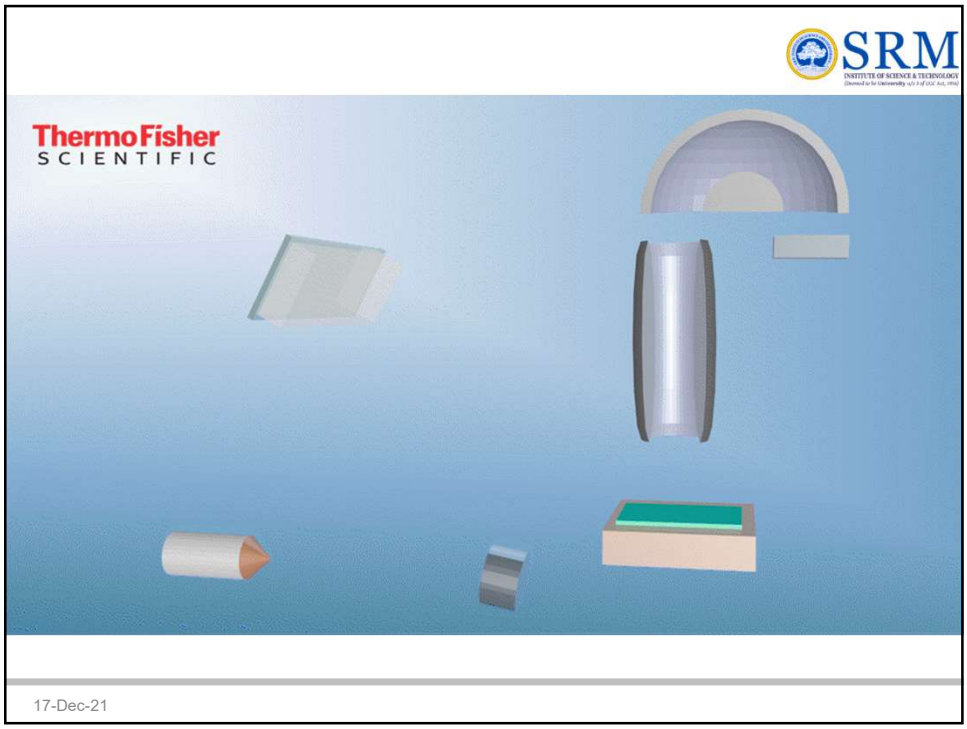

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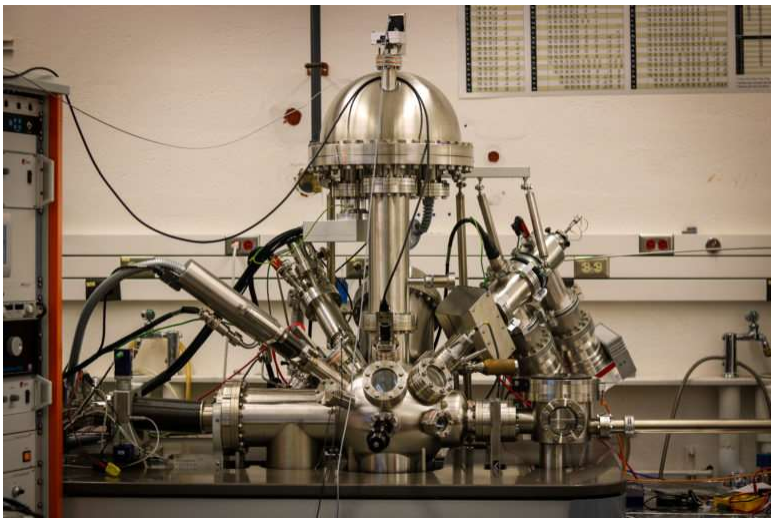
XPS Instrument



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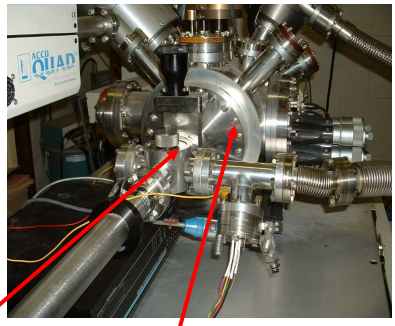
Sample introduction chamber

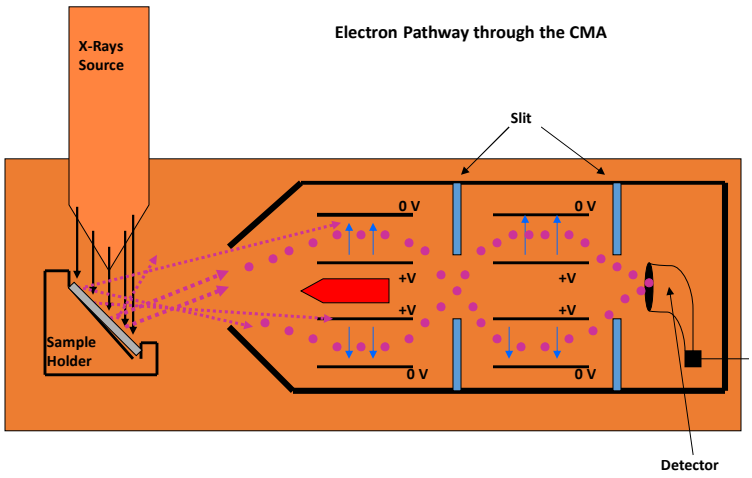
- The sample will be introduced through a chamber that is in contact with the outside environment
- It will be closed and pumped to low vacuum
- After the first chamber is at low vacuum the sample will be introduced into the second chamber in which a UHV environment exists



Cylindrical Mirror Analyzer (CMA)

- The electrons ejected will pass through a device called a CMA.
- The CMA has two concentric metal cylinders at different voltages.
- One of the metal cylinders will have a positive voltage and the other will have a 0 voltage. This will create an electric field between the two cylinders.

Cylindrical Mirror Analyzer (CMA)



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Cylindrical Mirror Analyzer (CMA)

- When the e-s pass through the metal cylinders, they will collide with one of the cylinders or they will just pass through.
  - If the e-'s velocity is too high it will collide with the outer cylinder
  - If is going too slow then will collide with the inner cylinder.
  - Only the e- with the right velocity will go through the cylinders to reach the detector.
- With a change in cylinder voltage the acceptable kinetic energy will change and then you can count how many e-s have that KE to reach the detector.

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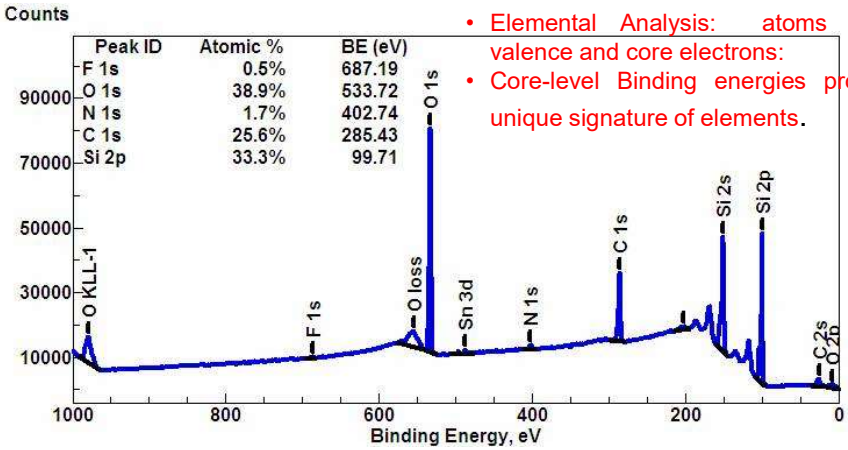
XPS spectrum



- Elemental Analysis: atoms have valence and core electrons:
- Core-level Binding energies provide unique signature of elements.

Wide-scan or survey spectrum of a somewhat **dirty silicon wafer**, showing all elements present. A survey spectrum is usually the starting point of most XPS analyses because it shows all elements present on the sample surface and allows one to set up subsequent high-resolution XPS spectra acquisition. The inset shows a quantification table **indicating all elements** observed, their binding energies, and their **atomic percentages**.

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XPS spectrum

- The XPS peaks **are sharp**
- A typical XPS spectrum is a plot of the **number of electrons detected (sometimes per unit time) (Y-axis, ordinate) versus the binding energy of the electrons** detected (X-axis, abscissa)
- Each element produces a **characteristic set of XPS peaks at characteristic binding energy values that directly identify each element** that exists in or on the surface of the material being analysed
- These characteristic spectral peaks correspond to the electron configuration of the electrons within the atoms, **e.g., 1s, 2s, 2p, 3s, etc**.

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Identification of XPS peaks

- The plot has **characteristic peaks for each element** found in the surface of the sample.
- There are **tables with the KE and BE already assigned** to each element.
- After the spectrum is plotted you can look for the designated value of the peak energy from the graph and find the element present on the surface.

How to interpret the data?

- Peaks from the XPS spectra **give relative number of electrons with a specific binding energy. The shorter the peak, the less electrons represented**
- For example, if a peak, ***A*, is half the height of another peak *B*, that means there were half as many electrons detected** with the binding energy at *A* compared to the number of electrons detected with the binding energy at *B*
- Therefore, the peak intensities **give information about the percent composition of a material**.

How to interpret the data?

- The **greater the binding energy, the greater the attraction of that electron to the nucleus**. i.e. peaks from electrons in **1s will have a greater energy** than peaks representing **electrons from 2s.**

- **Electrons in 2s will have greater energy than those in 2p.** Some instruments have peak identification features, but otherwise, the identification of peaks/lines on the spectra can be completed by looking at standards of different materials.

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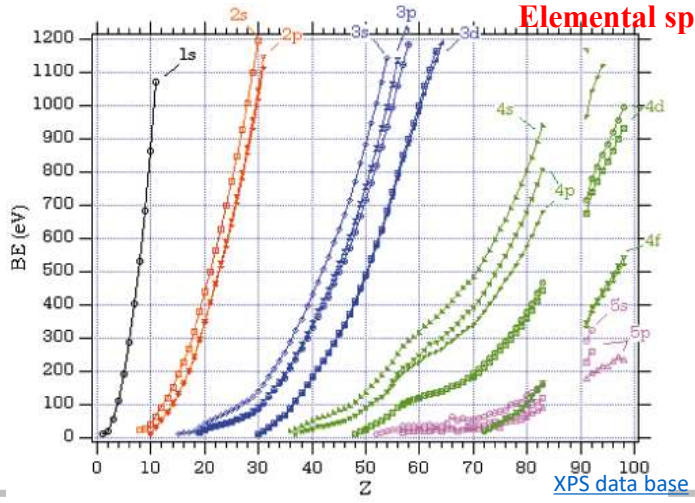
Z dependence

BE follows the energy levels: BE(1s)>BE(2s)>BE(2p)…
BE with same orbital increase with Z: BE(Mg1s)>BE(Na1s)

Elemental specific!



XPS data base

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XPS technology, analysis capabilities

- Considered as non-destructive
  - because it produces soft X-rays to induce photoelectron emission from the sample surface
- Provide information about surface layers or thin film structures
- Applications in the industry:
  - Polymer surface
  - Catalyst
  - Corrosion
  - Adhesion
  - Semiconductors
  - Dielectric materials
  - Electronics packaging
  - Magnetic media
  - Thin film coatings

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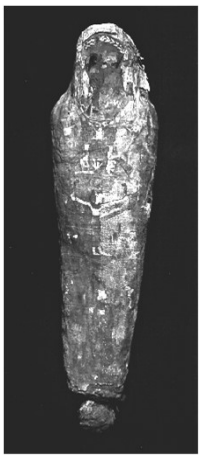
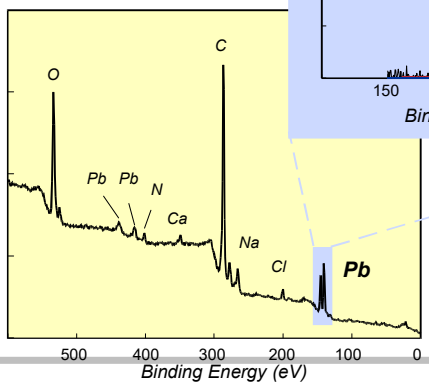
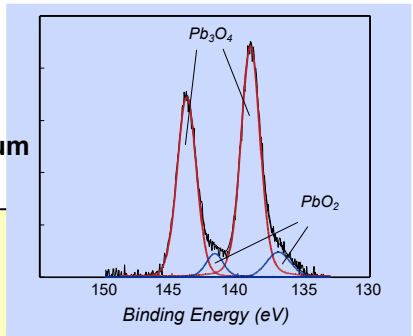
XPS analysis of pigment from mummy



Egyptian Mummy
2nd Century AD
World Heritage Museum
University of Illinois





XPS analysis showed that the pigment used on the mummy wrapping was Pb_3O_4 rather than Fe_2O_3

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Impurity analysis

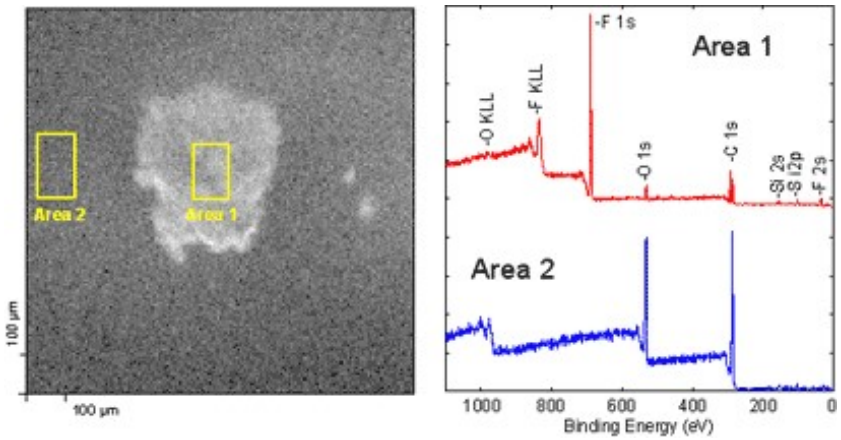

figure shows an impurity in the polymer surface that shows the presence of fluorine within it

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Chemical state identification

Core level chemical shifts:
For the same atom in two different chemical states:

$$\Delta BE = BE(2) - BE(1) = KE(1) - KE(2)$$

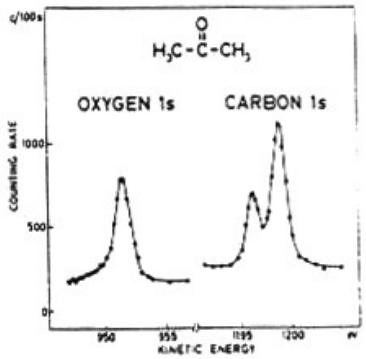

Fig. I:15. Electron spectrum of acetone with two carbon lines corresponding to differently bound carbon atoms. See also Sections V:1 and V:3c. This spectrum was recorded from acetone vapour irradiated with AlKα radiation.

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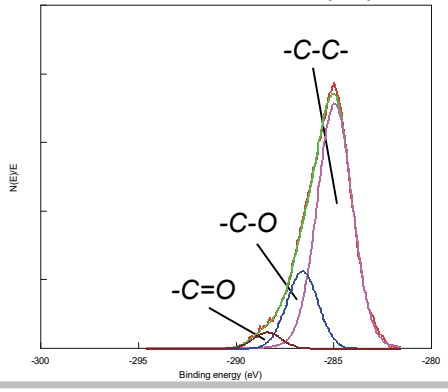
Analysis of Carbon Fiber-Polymer Composite Material by XPS

Woven carbon fiber composite

XPS analysis identifies the functional groups present on composite surface. Chemical nature of fiber-polymer interface will influence its properties.



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Summary of XPS capabilities

- Elemental analysis
- Chemical state information
- Quantification (sensitivity about 0.1 atomic %)
- Chemical mapping
- Depth profiling
- Ultrathin layer thickness
- Suitable for insulating samples
- Small area analysis (10 μm spatial resolution)
- Very expensive
- Time consuming

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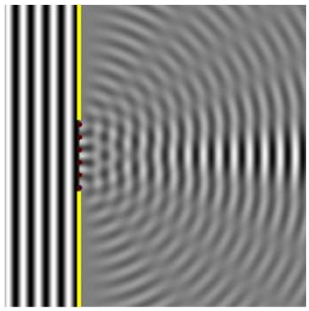
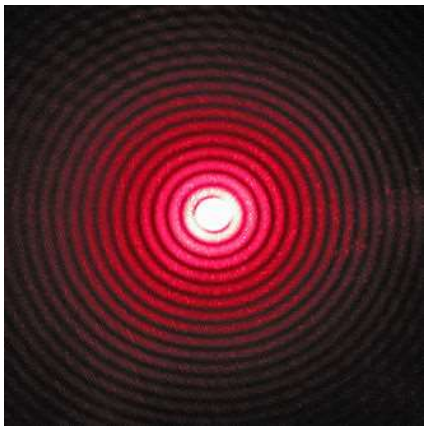
Diffraction of light by slits



- Incoming light is a plane wave
- Slit apertures result in an outgoing spherical wave. Interference determines the diffraction pattern

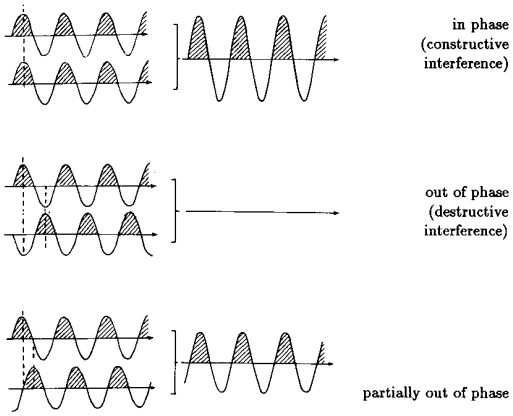


- Red laser beam' diffraction pattern projected onto a plate after passing through a small circular aperture in another plate

 "Crystal Structure Analysis for Chemists and Biologists", Glusker, Lewis and Rossi, VCH, 1994.

Adding wave functions

For electromagnetic radiation ***to be diffracted the spacing in the grating (grating refers to a series of obstacles or a series of scatterers) should be of the same order as the wavelength***



 "Crystal Structure Analysis for Chemists and Biologists", Glusker, Lewis and Rossi, VCH, 1994.

X-ray diffraction

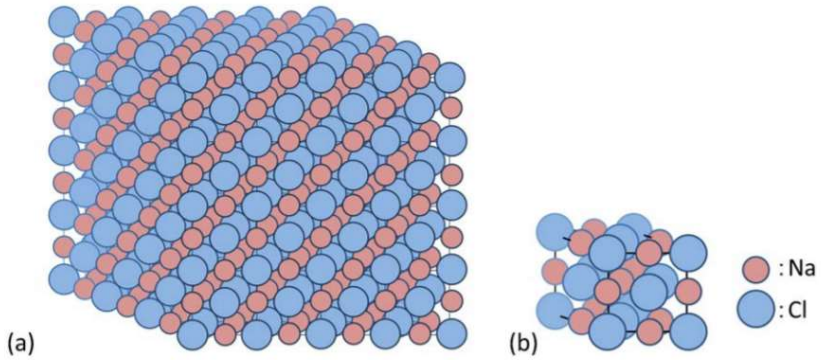
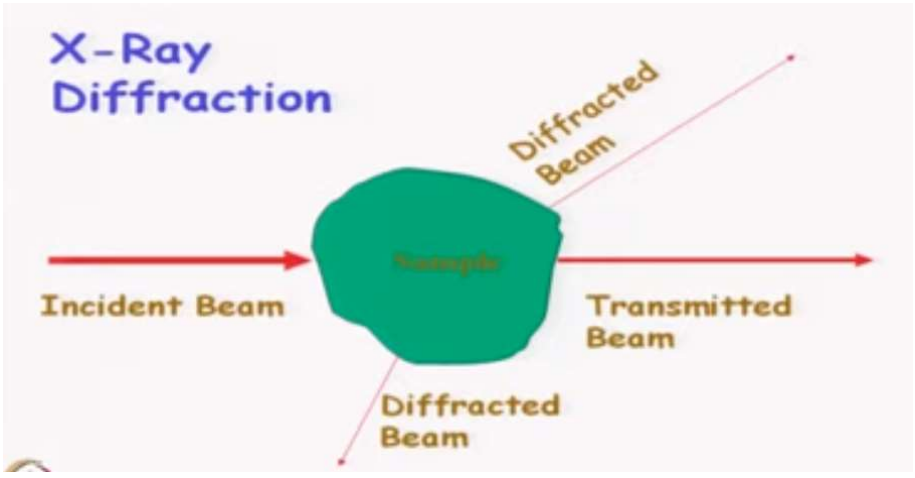


Fig. 1. (a) Structural model of NaCl crystal and (b) the structural unit.

X-ray diffraction



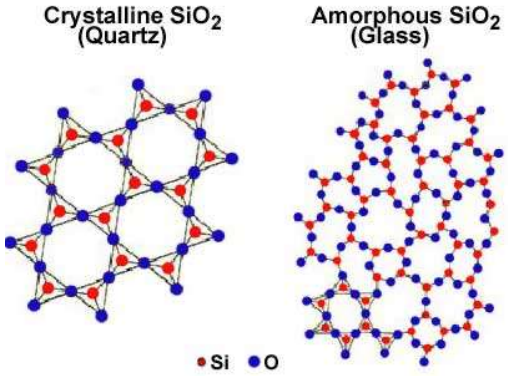
X-ray diffraction

- A beam of X-rays directed at a crystal interacts with the electrons of the atoms in the crystal.
- The electrons oscillate under the influence of the incoming X-rays and become secondary sources of EM radiation.
- The secondary radiation is in all directions.
- The waves emitted by the electrons have the same frequency as the incoming X-rays : coherent.
- The emission can undergo constructive or destructive interference.

X-ray diffraction

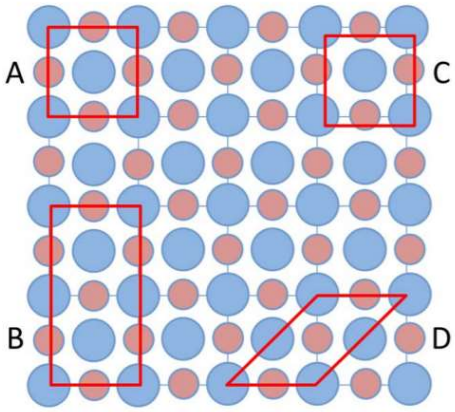
- "Scattering of X-rays by the atoms of a crystal that produces an interference effect so that the diffraction pattern gives **information on the structure of the crystal or the identity of a crystalline substance**"
  - Both visible light and X-rays are electromagnetic radiation – the only difference lies in the wavelength!
- **X-ray diffraction can be envisioned as an equivalent process to what happens when you shine light through a grating**
  - Formulism obeys the same laws as "slit experiments"

Types of solids



Unit Cell: A volume of the crystal that, via pure translational repetition, generates the entire crystal without overlaps or voids.

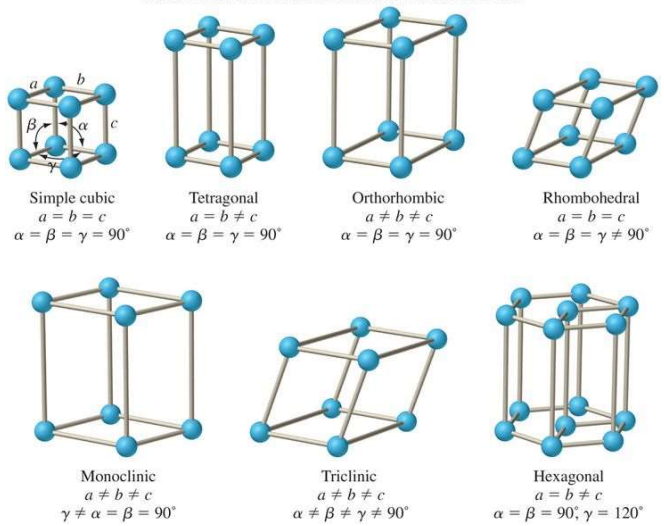
X-ray diffraction



Two-dimensional structure of NaCl and various ways of finding structural units.

- **Crystals consist of planes of atoms that are spaced a distance d apart**, but can be resolved into many atomic planes, each with a different d-spacing.
- **a,b and c (length) and α, β and γ (angles between a,b and c) are lattice constants or parameters**

Crystal structures



Simple cubic
$a = b = c$
$\alpha = \beta = \gamma = 90^\circ$

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

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

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

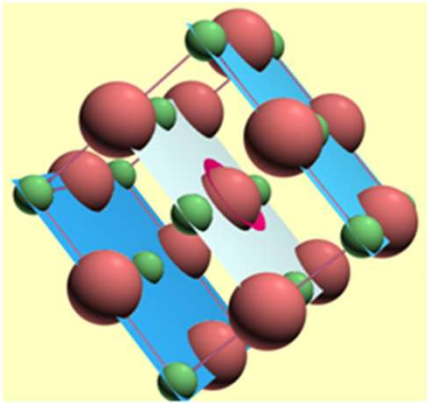
Monoclinic
$a \neq b \neq c$
$\gamma \neq \alpha = \beta = 90^\circ$

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

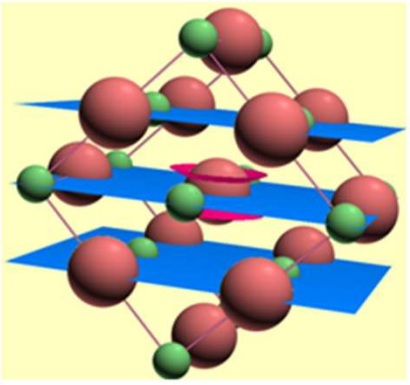
Hexagonal
$a = b \neq c$
$\alpha = \beta = 90^\circ, \gamma = 120^\circ$

X-ray diffraction

The (200) planes of atoms in NaCl

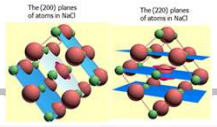


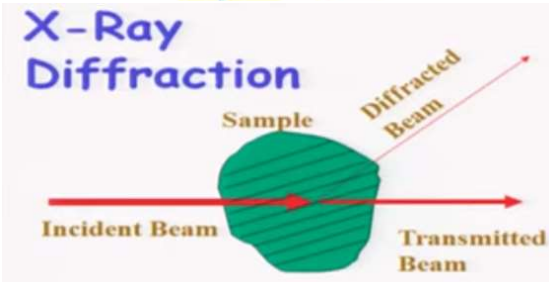
The (220) planes of atoms in NaCl



X-ray diffraction

- Atoms in a crystal form a periodic array of coherent scatterers
  - **The wavelength of X-rays are similar to the distance between atoms**
  - **Diffraction from different planes of atoms produces a diffraction pattern, which contains information about the atomic arrangement within the crystal**
- X-rays are also reflected, scattered incoherently, absorbed, refracted, and transmitted when they interact with matter.

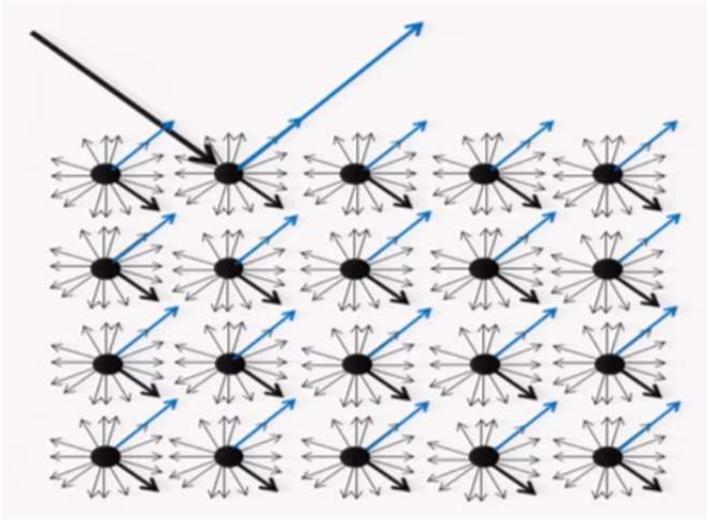




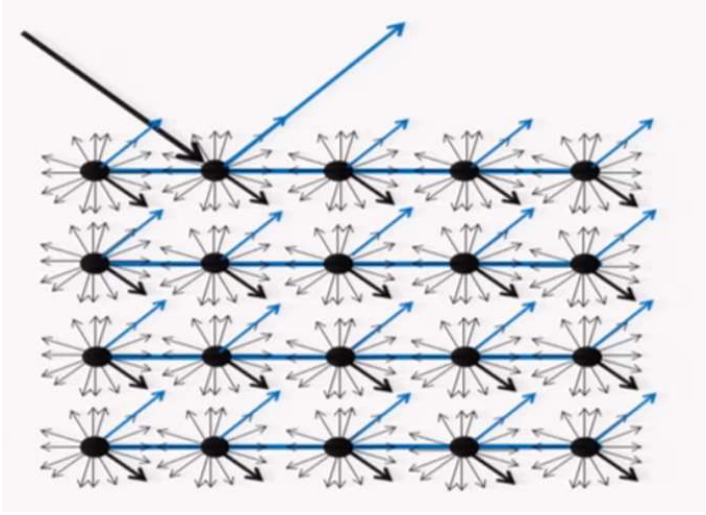
Bragg Reflection

Bragg's Law (Part I): For every diffracted beam there exists a set of crystal lattice planes such that the diffracted beam appears to be specularly reflected from this set of planes.

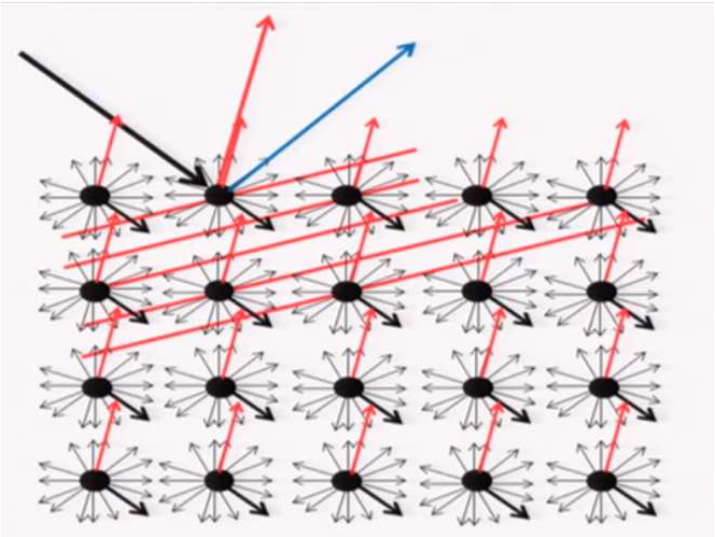
X-ray diffraction



X-ray diffraction



X-ray diffraction



What is Bragg's Law?

- Bragg's Law refers to the simple equation: **$n\lambda = 2d \sin\theta$** derived by the English physicists Sir W.H. Bragg and his son Sir W.L. Bragg in 1913.
- The **variable *d* is the distance between atomic layers** in a crystal, and the variable lambda is the **wavelength** of the incident X-ray beam, n is an integer.
- The Braggs were awarded the **Nobel Prize in physics in 1915** for their work in determining crystal structures beginning with NaCl, ZnS and diamond.
- **When a monochromatic X-rays are incident upon a crystal, atoms in different layers acts as a source of scattering radiation of same wavelength.**

What is Bragg's Law?

- **Bragg diffraction occurs when radiation, with a wavelength comparable to atomic spacings, is scattered in a specular fashion by the atoms of a crystalline system, and undergoes constructive interference**
- When the scattered **waves interfere constructively, they remain in phase** since the difference between the path lengths of the two waves **is equal to an integer multiple of the wavelength**
- The path difference between two waves undergoing interference is given by $2d\sin\theta$, where θ is the scattering angle .

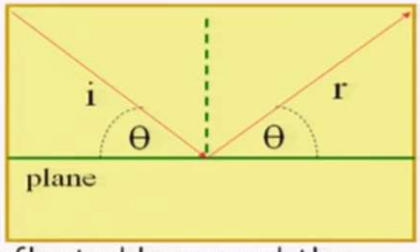
X-ray diffraction

X-Ray Diffraction

Bragg's Law (Part 1): the diffracted beam appears to be **specularly** reflected from a set of crystal lattice planes.

Specular reflection:

(A) Angle of incidence =Angle of reflection (both measured from the plane and not from the normal)



(B) The incident beam, the reflected beam and the plane normal lie in one plane

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

Constructive interference occurs only when

$n\lambda = AB + BC$

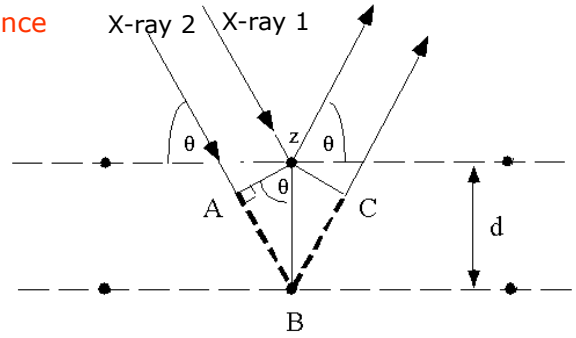
$AB=BC$

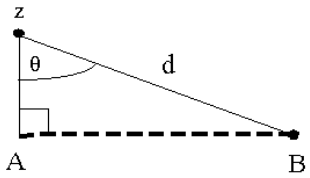
$n\lambda = 2AB$

$\sin\theta=AB/d$

$AB=d\sin\theta$

$n\lambda =2d\sin\theta$





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

n – integer, called the order of diffraction

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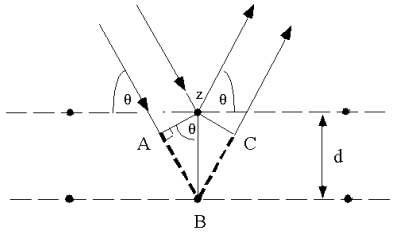
Deriving Bragg's Law



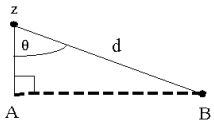


Fig. 1 Deriving Bragg's Law using the reflection geometry and applying trigonometry. The lower beam must travel the extra distance (AB + BC) to continue traveling parallel and adjacent to the top beam.

Bragg's Law can easily be derived by considering the conditions necessary to make the phases of the beams coincide when the incident angle equals and reflecting angle. The rays of the incident beam are always in phase and parallel up to the point at which the top beam strikes the top layer at atom z (Fig. 1). The second beam continues to the next layer where it is scattered by atom B. **The second beam must travel the extra distance AB + BC if the two beams are to continue traveling adjacent and parallel.** This extra distance must be an integral (n) multiple of the wavelength (λ) for the phases of the two beams to be the same:

$n\lambda = AB + BC$ (2).

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Deriving Bragg's Law (cont.)

Recognizing d as the hypotenuse of the right triangle ABZ, we can use trigonometry to relate d and Θ to the distance (AB + BC). The distance AB is opposite Θ so,

AB = d sinΘ(3).

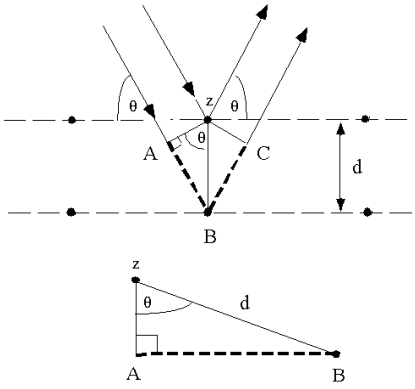
Because AB = BC eq. (2) becomes,

nλ = 2AB (4)

Substituting eq. (3) in eq. (4) we have,

nλ = 2 d sinΘ, (1)

and Bragg's Law has been derived. The location of the surface does not change the derivation of Bragg's Law.



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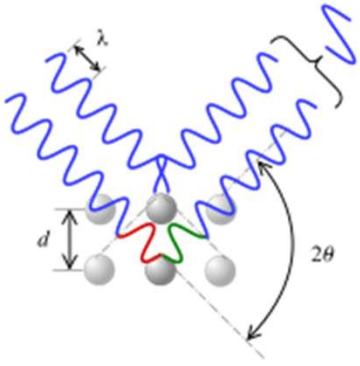
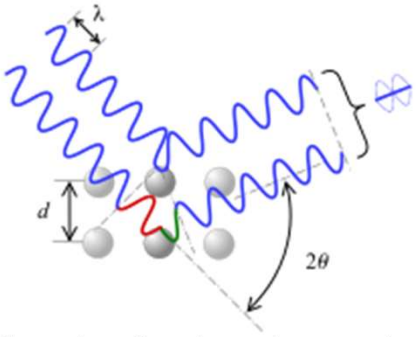
X-ray diffraction



If after reflection emerging waves are in phase, reflected intensity will be observed, ie, Bragg's Law is fulfilled.



If emerging reflected waves have opposite phase, no reflected intensity will be observed, ie, Bragg's Law is not fulfilled.

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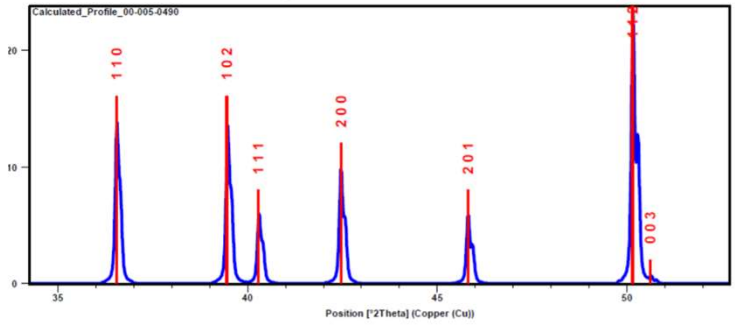
X-ray diffraction

- The **d-spacing** can described as the distance between planes of atoms that give rise to diffraction peaks.
- Each **peak in a diffractogram results from a corresponding d-spacing**.
- The planes of atoms can be referred to a 3D coordinate system and so can be described as a direction within the crystal.
- So d-spacing as well as having a dimension, usually quoted in Angstroms, can labelled **with a plane direction hkl.**
- This is why there is a subscript, it refers to a distance in that plane.

X-ray diffractogram

Diffraction pattern calculations treat a crystal as a collection of planes of atoms



- Each diffraction peak is attributed to the scattering from a specific set of parallel planes of atoms.
- Miller indices (hkl) are used to identify the different planes of atoms
- Observed diffraction peaks can be related to planes of atoms to assist in analyzing the atomic structure and microstructure of a sample

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X-ray diffractogram

- **Possible 2-THETA values where we can have reflections are determined by the unit cell dimensions**.
- However, the **intensities of the reflections are determined by the distribution of the electrons** in the unit cell.
- The **highest electron density are found around atoms**.
- Therefore, the intensities depend on what kind of atoms we have and where in the unit cell they are located.
- Planes **going through areas with high electron density will reflect strongly, planes with low electron density will give weak intensities**.

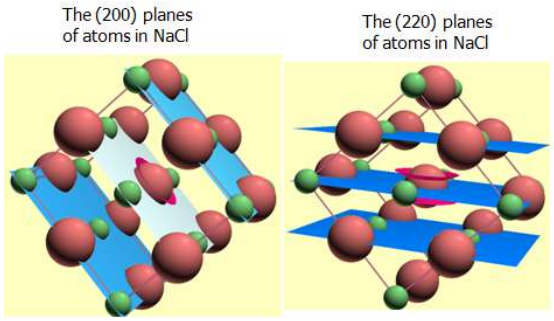
X-ray diffractogram

- **How to use Bragg's Law and a diffraction pattern to identify a mineral?**
- **In Bragg's law:** : **$n\lambda = 2d \sin\theta$**
  1. *We know lambda (the wavelength) = 1.54 angstrom and we assume n=1.*

  2. We can measure 2-theta from the diffraction pattern. divided by 2, these values become theta.

  3. That leaves us with an equation with one unknown -d- the d-spacing we want to find out.
- Peak at 23.04 degrees 2-theta corresponds to a d-spacing of 3.86 angstrom.
- peak at 39.37 degrees 2-theta. This corresponds to a d-spacing of 2.287 angstrom.

MILLER INDICES



- The 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
- These crystallographic planes are identified by Miller indices

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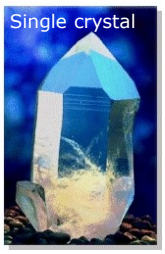
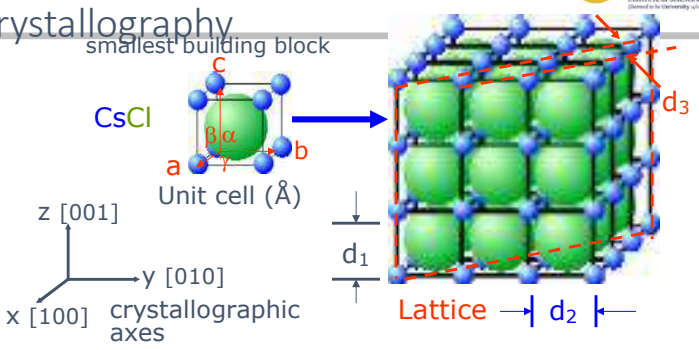
Basics of Crystallography





- A crystal consists of a periodic arrangement of the unit cell into a lattice. The unit cell can contain a single atom or atoms in a fixed arrangement.
- Crystals consist of planes of atoms that are spaced a distance d apart, but can be resolved into many atomic planes, each with a different d-spacing.
- a,b and c (length) and α, β and γ (angles between a,b and c) are lattice constants or parameters which can be determined by XRD.

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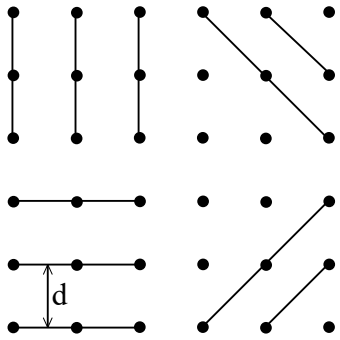
MILLER INDICES

- The crystal lattice may be regarded as made up of an **infinite set of parallel equidistant planes** passing through the lattice points which are known as lattice planes.
- In simple terms, the planes passing through lattice points are called '***lattice planes***'.
- For a given lattice, the lattice planes can be **chosen in a different number of ways.**



DIFFERENT LATTICE PLANES

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MILLER INDICES

- The orientation of planes or faces in a crystal can be **described in terms of their intercepts on the three axes**.
- Miller introduced a system to designate a plane in a crystal.
- He introduced a **set of three numbers** to specify a plane in a crystal.
- This set of three numbers is known as '***Miller Indices***' of the concerned plane.
- Miller indices is **defined as the reciprocals of the intercepts made by the plane on the three axes**.

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Procedure for finding Miller Indices

- **Step 1:** Determine the intercepts of the plane along the axes X,Y and Z in terms of the lattice constants a,b and c.
- **Step 2:** Determine the reciprocals of these numbers.
- **Step 3:** Find the least (lowest) common denominator (*lcd*) and multiply each by this *lcd*.
- **Step 4:**The result is written in parenthesis. This is called the `Miller Indices' of the plane in the form (h k l).

DETERMINATION OF 'MILLER INDICES'

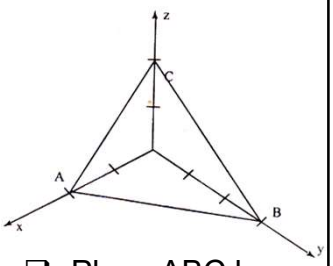
Step 1: The intercepts are 2,3 and 2 on the three axes.

Step 2: The reciprocals are 1/2, 1/3 and 1/2.

Step 3: The least common denominator is '6'. Multiplying each reciprocal by lcd, we get, 3,2 and 3.

Step 4: Miller indices for the plane ABC is (3 2 3)

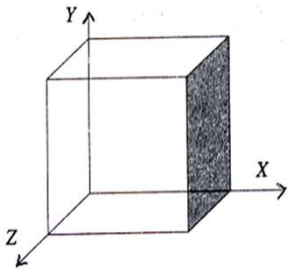
PLANES IN A CRYSTAL



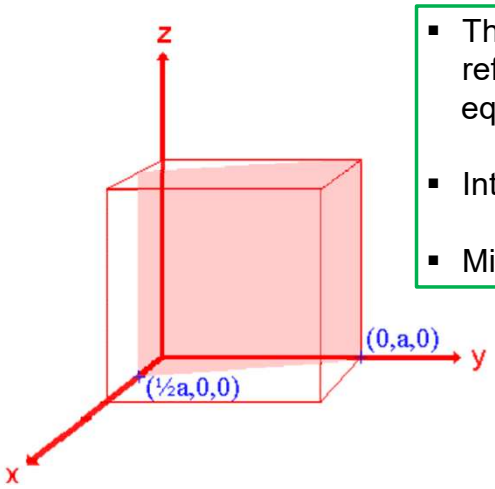
- Plane ABC has intercepts of 2 units along X-axis, 3 units along Y-axis and 2 units along Z-axis.

DETERMINATION OF 'MILLER INDICES'

- In the above plane, the intercept along X axis is 1 unit. The plane is parallel to Y and Z axes. So, the intercepts along Y and Z axes are '∞'.
- Now the intercepts are 1, ∞ and ∞. The reciprocals of the intercepts are = 1/1, 1/∞ and 1/∞.
- Therefore the Miller indices for the above plane is (1 0 0)
- A plane which is parallel to any one of the co-ordinate axes has an intercept of infinity (∞). Therefore the Miller index for that axis is zero; i.e. for an intercept at infinity, the corresponding index is zero



DETERMINATION OF 'MILLER INDICES'



- This plane cuts two of the reference axes, but not equidimensionally
- Intercepts: (½, 1, 0)
- Miller indices : (2 1 0)

IMPORTANT FEATURES OF MILLER INDICES

- It is only the ratio of the indices which is important in this notation. The (6 2 2) planes are the same as (3 1 1) planes
- If a plane cuts an axis on the negative side of the origin, corresponding index is negative. It is represented by a bar, like ($\bar{1}$ 0 0). i.e. Miller indices ($\bar{1}$ 0 0) indicates that the plane has an intercept in the –ve X –axis.

Calculate the miller indices for the plane with intercepts 2a, - 3b and 4c the along the crystallographic axes.

The intercepts are 2, - 3 and 4

Step 1: The intercepts are 2, -3 and 4 along the 3 axes

Step 2: The reciprocals are

Step 3: The least common denominator is 12.

Multiplying each reciprocal by lcd, we get 6 -4 and 3

Step 4: Hence the Miller indices for the plane is $(6\ \bar{4}\ 3)$

Relation between d and a

The relation between the interplanar distance and the interatomic distance is given by,

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$ for cubic crystal.

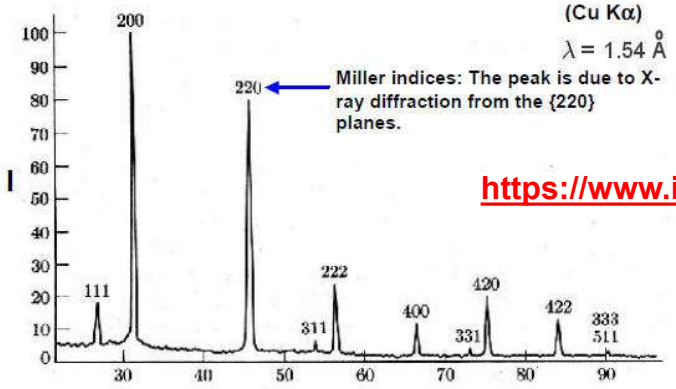
The lattice constant for a unit cell of aluminum is 4.031Å
Calculate the interplanar space of (2 1 1) plane.

a = 4.031 Å
(h k l) = (2 1 1)
Interplanar spacing

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = \frac{4.031 \times 10^{-10}}{\sqrt{2^2 + 1^2 + 1^2}}$$

∴ **d = 1.6456 Å**

XRD Pattern of NaCl Powder



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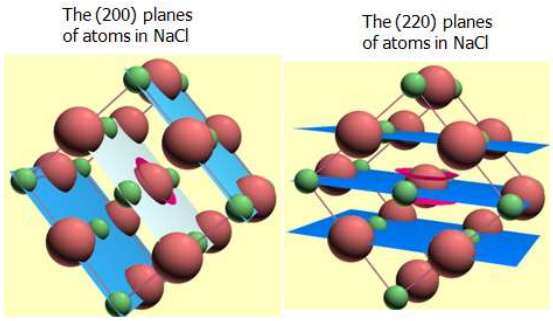
X-ray and atom(s)



- The 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
- These crystallographic planes are identified by Miller indices

17-Dec-21

X-ray diffractogram

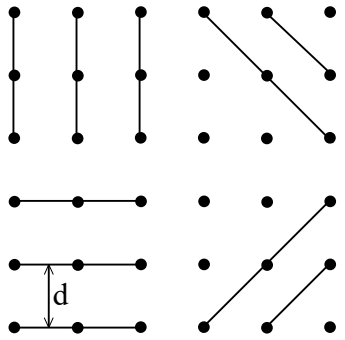
- **Possible 2-THETA values where we can have reflections are determined by the unit cell dimensions**.
- However, the **intensities of the reflections are determined by the distribution of the electrons** in the unit cell.
- The **highest electron density are found around atoms**.
- Therefore, the intensities depend on what kind of atoms we have and where in the unit cell they are located.
- Planes **going through areas with high electron density will reflect strongly, planes with low electron density will give weak intensities**.

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

17-Dec-21

MILLER INDICES

- The crystal lattice may be regarded as made up of an **infinite set of parallel equidistant planes** passing through the lattice points which are known as lattice planes.
- In simple terms, the planes passing through lattice points are called '***lattice planes***'.
- For a given lattice, the lattice planes can be **chosen in a different number of ways.**



DIFFERENT LATTICE PLANES

17-Dec-21

MILLER INDICES

- The orientation of planes or faces in a crystal can be **described in terms of their intercepts on the three axes**.
- Miller introduced a system to designate a plane in a crystal.
- He introduced a **set of three numbers** to specify a plane in a crystal.
- This set of three numbers is known as '***Miller Indices***' of the concerned plane.
- Miller indices is **defined as the reciprocals of the intercepts made by the plane on the three axes**.

17-Dec-21

Procedure for finding Miller Indices

- **Step 1:** Determine the intercepts of the plane along the axes X,Y and Z in terms of the lattice constants a,b and c.
- **Step 2:** Determine the reciprocals of these numbers.
- **Step 3:** Find the least (lowest) common denominator (*lcd*) and multiply each by this *lcd*.
- **Step 4:**The result is written in parenthesis. This is called the `Miller Indices' of the plane in the form (h k l).

DETERMINATION OF 'MILLER INDICES'

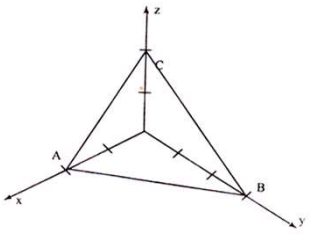
Step 1: The intercepts are 2,3 and 2 on the three axes.

Step 2: The reciprocals are 1/2, 1/3 and 1/2.

Step 3: The least common denominator is '6'. Multiplying each reciprocal by lcd, we get, 3,2 and 3.

Step 4: Miller indices for the plane ABC is (3 2 3)

PLANES IN A CRYSTAL



- Plane ABC has intercepts of 2 units along X-axis, 3 units along Y-axis and 2 units along Z-axis.

DETERMINATION OF 'MILLER INDICES'

- In the above plane, the intercept along X axis is 1 unit. The plane is parallel to Y and Z axes. So, the intercepts along Y and Z axes are '∞'.
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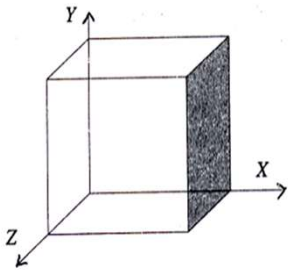

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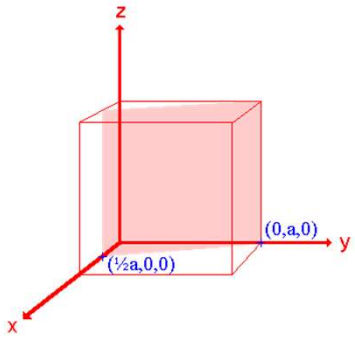

- Intercepts: ½ , 1 , ∞
- Reciprocals: 2, 1 , 0
- Miller Indices: (210)

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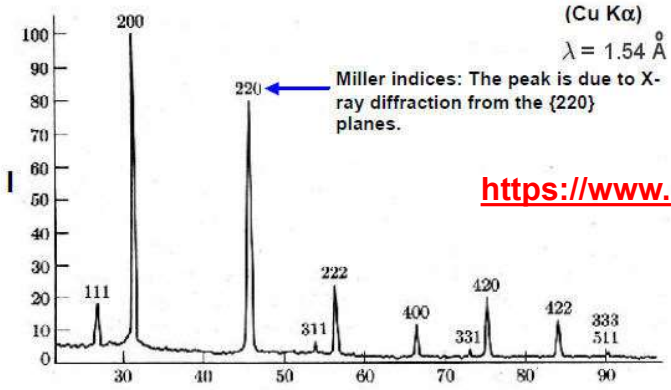
XRD Pattern of NaCl Powder



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Thank you all for your attention

Information presented here were collected from various sources – textbooks, articles, manuscripts, internet and newsletters. All the researchers and authors of the above mentioned sources are greatly acknowledged.