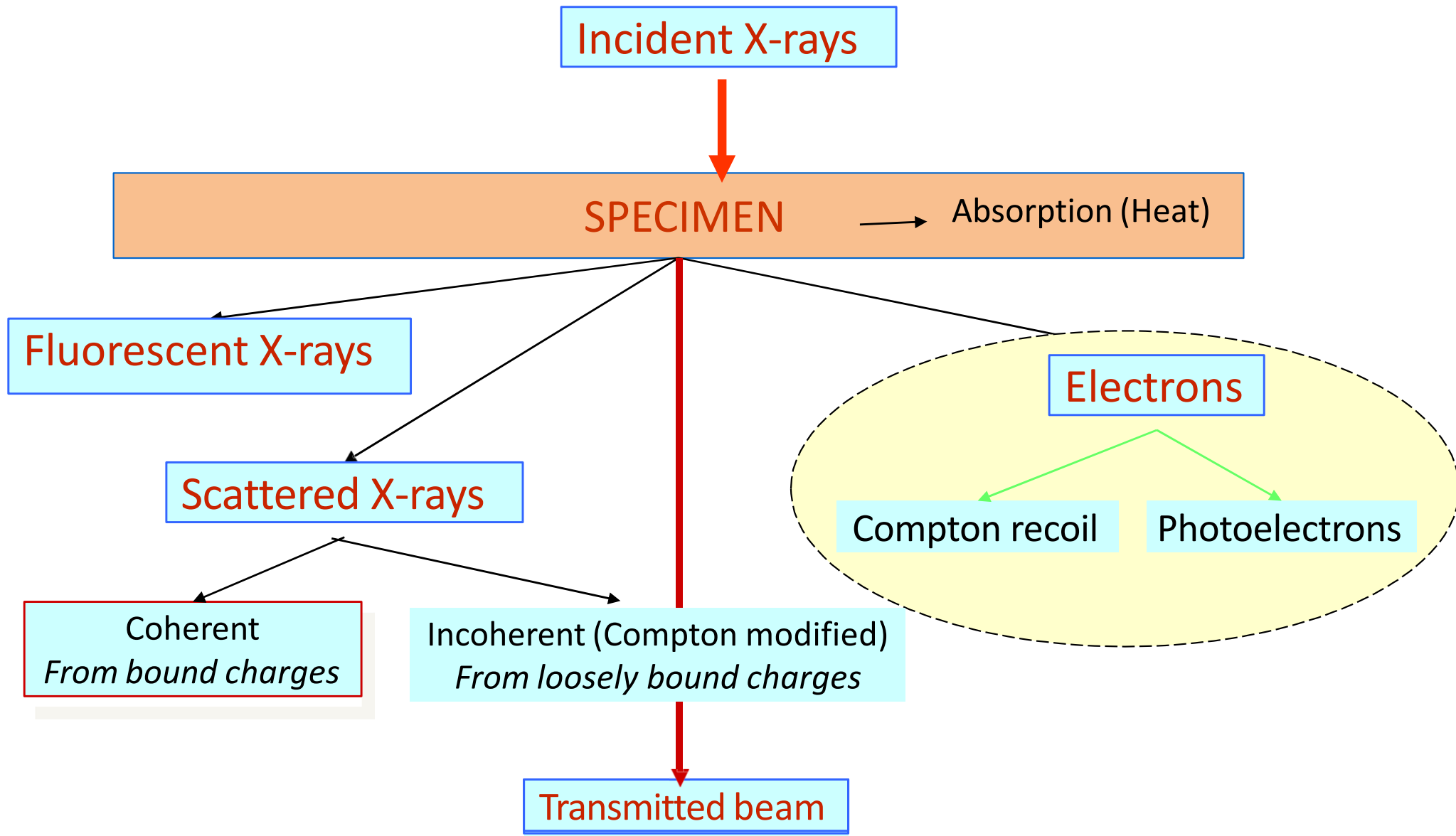# DEPARTMENT OF PHYSICS AND NANOTECHNOLOGY
SRM INSTITUTE OF SCIENCE AND TECHNOLOGY

Lecture-9

Characterization Techniques-X-Ray Diffraction-Powder Method
and XPS

Interaction of X-rays with matter

Incident X-rays

↓

SPECIMEN → Absorption (Heat)

Fluorescent X-rays

Scattered X-rays

Coherent
From bound charges

Incoherent (Compton modified)
From loosely bound charges

Transmitted beam

Electrons

Compton recoil   Photoelectrons

The coherently scattered X-rays are the ones that are important from XRD perspective.

Bragg's Law

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

English physicists Sir W.H. Bragg and his son Sir W.L. Bragg developed a relationship in 1913 to explain why the cleavage faces of crystals appear to reflect X-ray beams at certain angles of incidence (theta, θ). The variable d is the distance between atomic layers in a crystal, and the variable lambda λ is the **wavelength** of the incident X-ray beam; n is an integer. This observation is an example of X-ray **wave interference** (Roentgenstrahlinterferenzen), commonly known as X-ray diffraction (XRD), and was direct evidence for the periodic atomic structure of crystals postulated for several centuries.

Bragg's Law

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

Sir William Henry Bragg
① 1/2 of the prize
United Kingdom

London University
London, United Kingdom

b. 1862
d. 1942

William Lawrence Bragg
① 1/2 of the prize
United Kingdom

Victoria University
Manchester, United Kingdom

b. 1890
(in Adelaide, Australia)
d. 1971

The Braggs were awarded the Nobel Prize in physics in 1915 for their work in determining crystal structures beginning with NaCl, ZnS and diamond.

Although Bragg's law was used to explain the interference pattern of X-rays scattered by crystals, diffraction has been developed to study the structure of all states of matter with any beam, e.g., ions, electrons, neutrons, and protons, with a wavelength similar to the distance between the atomic or molecular structures of interest.

X-Ray Diffraction

➢X-ray diffraction is used for the complete determination of molecular structure of crystals.

➢Every lattice plane in a crystal behaves like diffraction grating, on the exposure of X-rays.

➢The position of the spectral lines when diffracted depends on the distance between successive lines; similarly the nature of the X-ray diffracted by a crystal is determined by the spacing between successive planes.

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

Constructive interference occurs only when

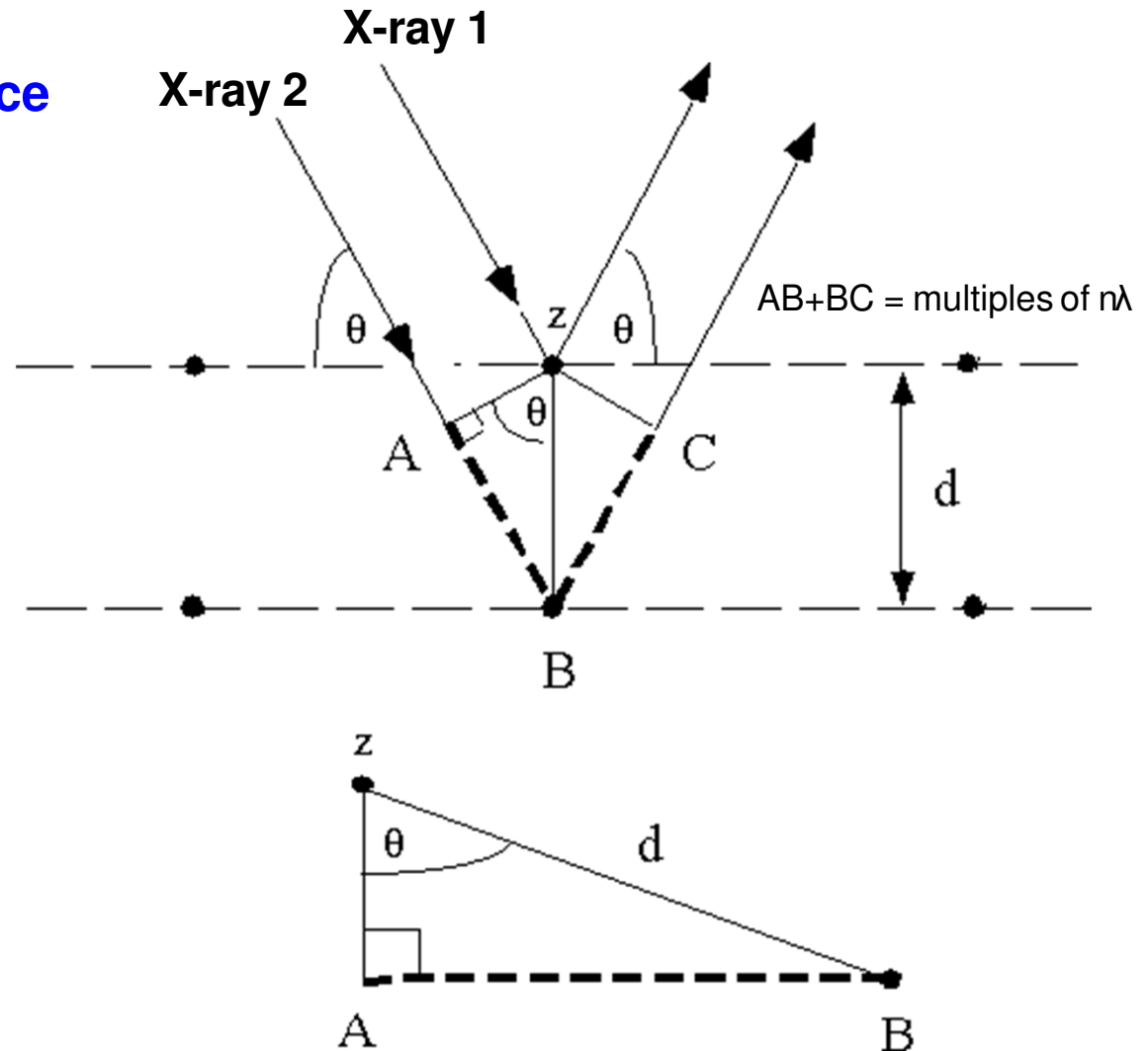**N λ = AB + BC**

AB=BC

N λ = 2AB

Sinθ=AB/d

AB= d sin θ

N λ = 2d sin θ

N λ= 2d$_{hkl}$sinθ_{hkl}

X-ray 1

X-ray 2

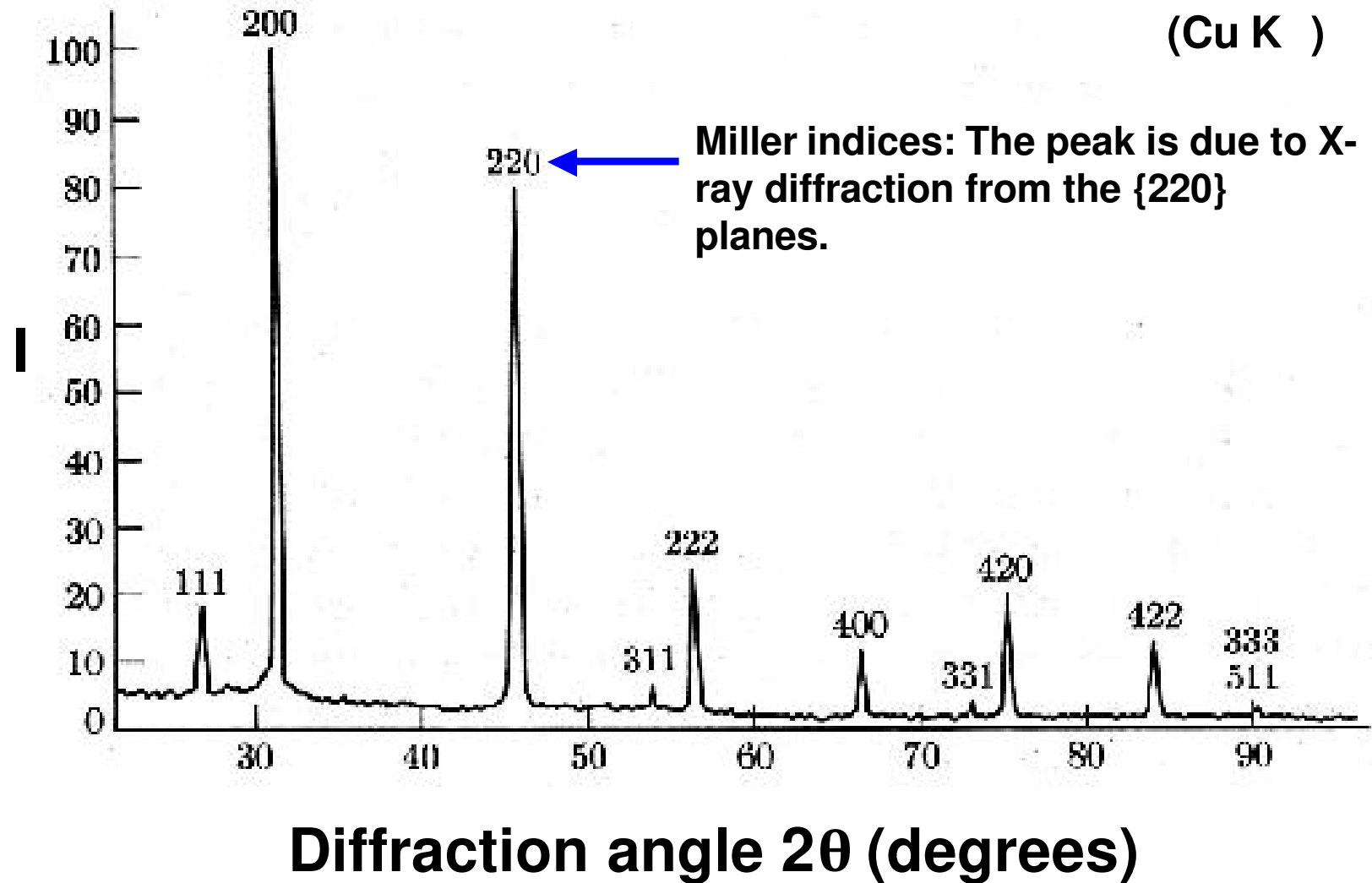AB+BC = multiples of nλ

X-rays scatter from atoms in a material and therefore contain information about the atomic arrangement
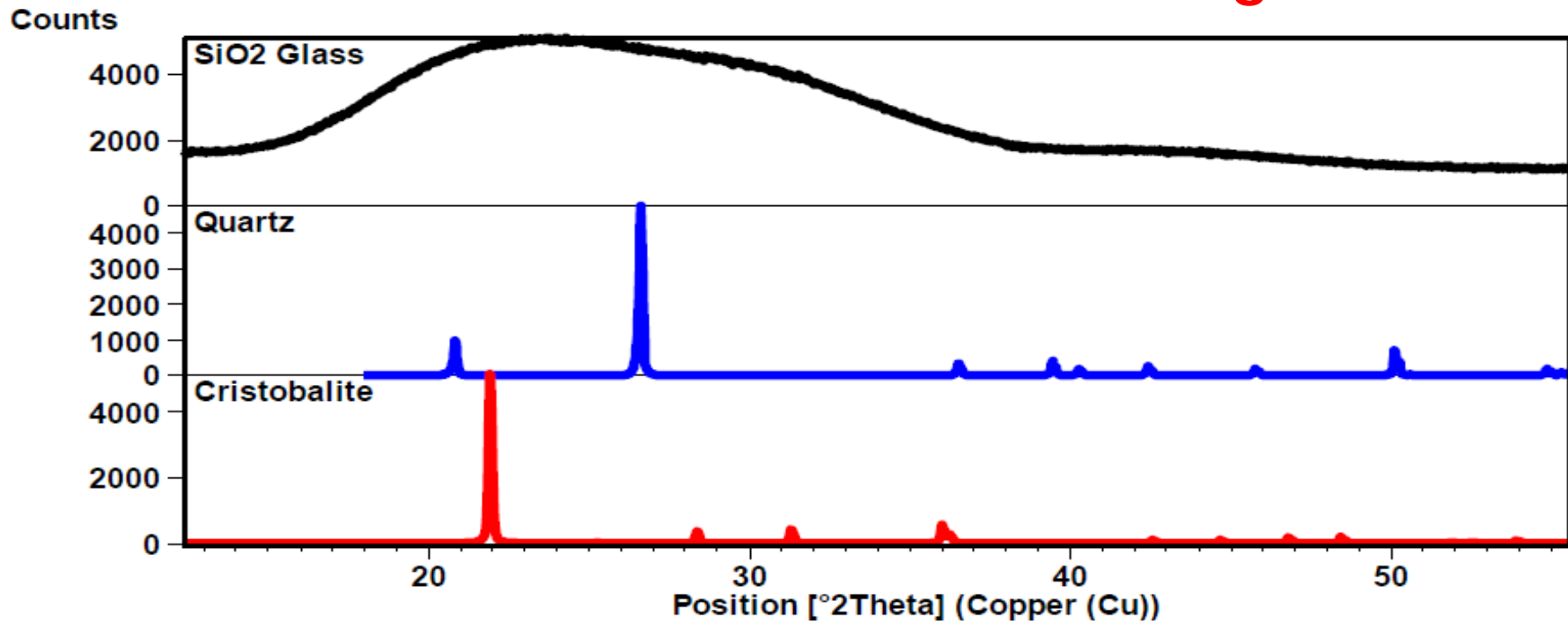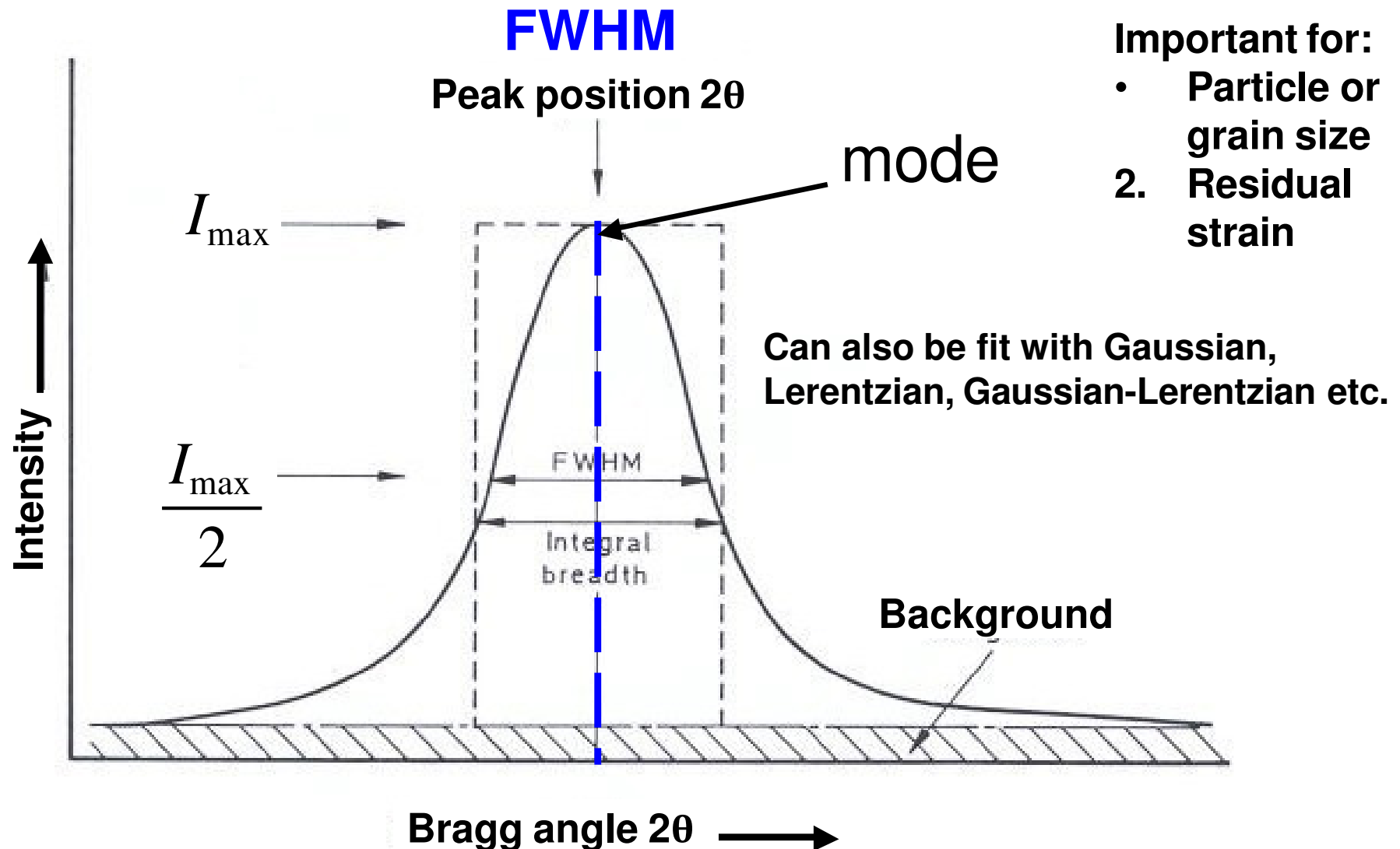

- The three X-ray scattering patterns above were produced by three *chemically identical forms SiO$_2$*
- Crystalline materials like quartz and Cristobalite produce X-ray diffraction patterns
  - Quartz and Cristobalite have two different crystal structures
  - The Si and O atoms are arranged differently, but both have long-range atomic order
  - The difference in their crystal structure is reflected in their different diffraction patterns
- The amorphous glass does not have long-range atomic order and therefore produces only broad scattering features
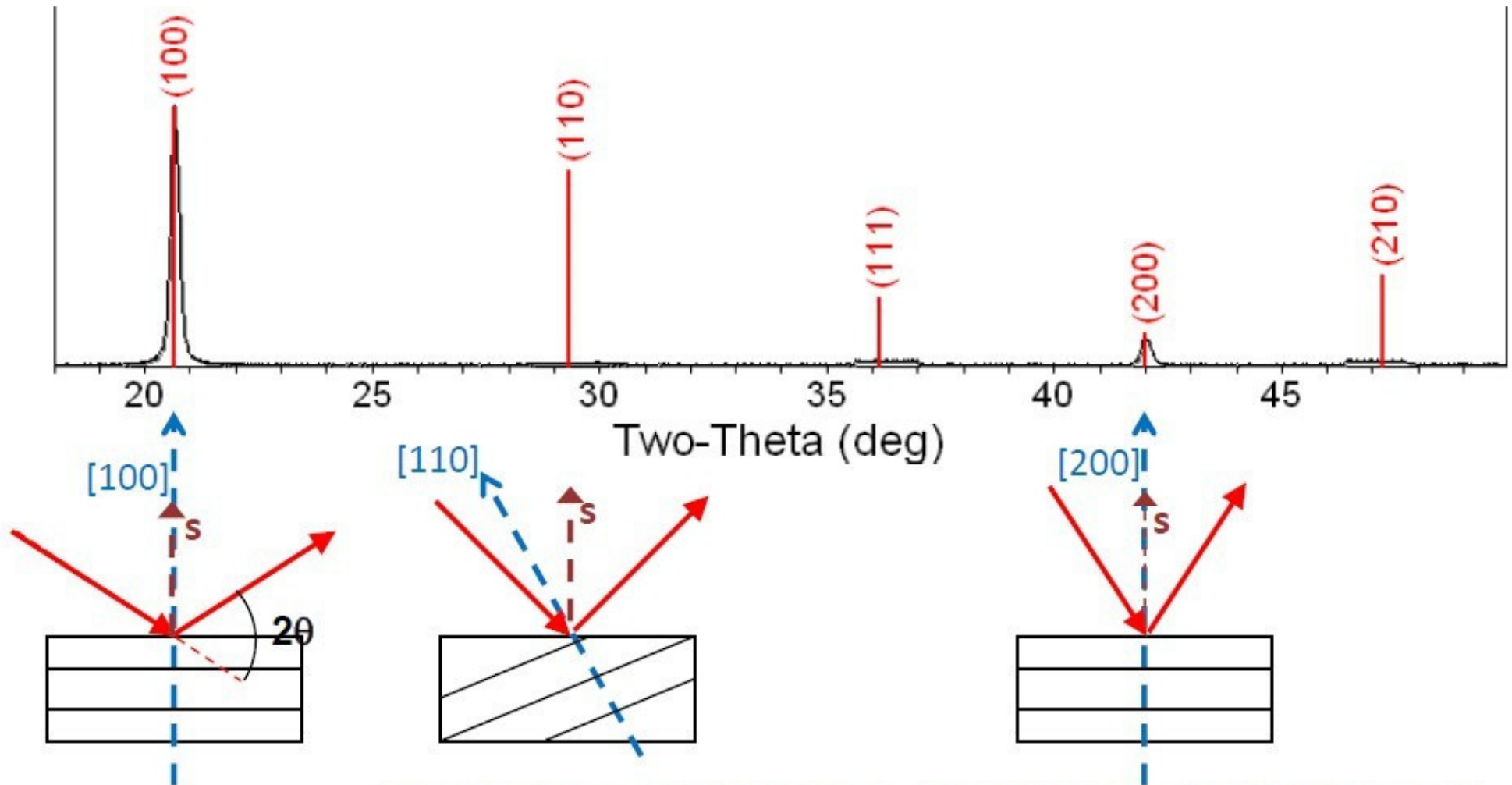
XRD Pattern of NaCl Powder

(Cu Kα)

Miller indices: The peak is due to X-ray diffraction from the {220} planes.

Diffraction angle 2θ (degrees)

Peak Width-Full Width at Half Maximum

A single crystal specimen in a Bragg-Brentano diffractometer would produce only one family of peaks in the diffraction pattern

At 20.6 °2θ, Bragg's law fulfilled for the (100) planes, producing a diffraction peak.

The (110) planes would diffract at 29.3 °2θ; however, they are not properly aligned to produce a diffraction peak (the perpendicular to those planes does not bisect the incident and diffracted beams). Only background is observed.

The (200) planes are parallel to the (100) planes. Therefore, they also diffract for this crystal. Since d_{200} is ½ d_{100}, they appear at 42 °2θ.

If a beam of monochromatic X-rays is incident on a crystal at an angle θ, some of the rays will be diffracted by the layers of atoms in the crystal.

The path length FC′D is larger than FCD by AC′B which is equal to 2AC′, and since AC′ = dsinθ, the path difference is 2dsinθ.
This difference in path length must be an integral number (n) of wavelengths (λ) for maximum diffraction of X-rays with destructive interference. Thus

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

which is the **Bragg's equation**.

With the help of the Bragg's equation it is possible to determine the spacing d between successive lattice planes, if λ is known and θ is measured.

The powder method:

➢A narrow beam of monochromatic X-rays fall on the finely powdered specimen to be examined, and the diffracted rays are passed on to a strip of film which almost completely surrounds the specimen.

➢The random orientation of crystals produces diffraction rings.

➢This method is commonly used for identification purposes by comparing the data with the standard files available.

➢For a cubic crystal the identification of lines in the powder photograph is simple compared to other types.
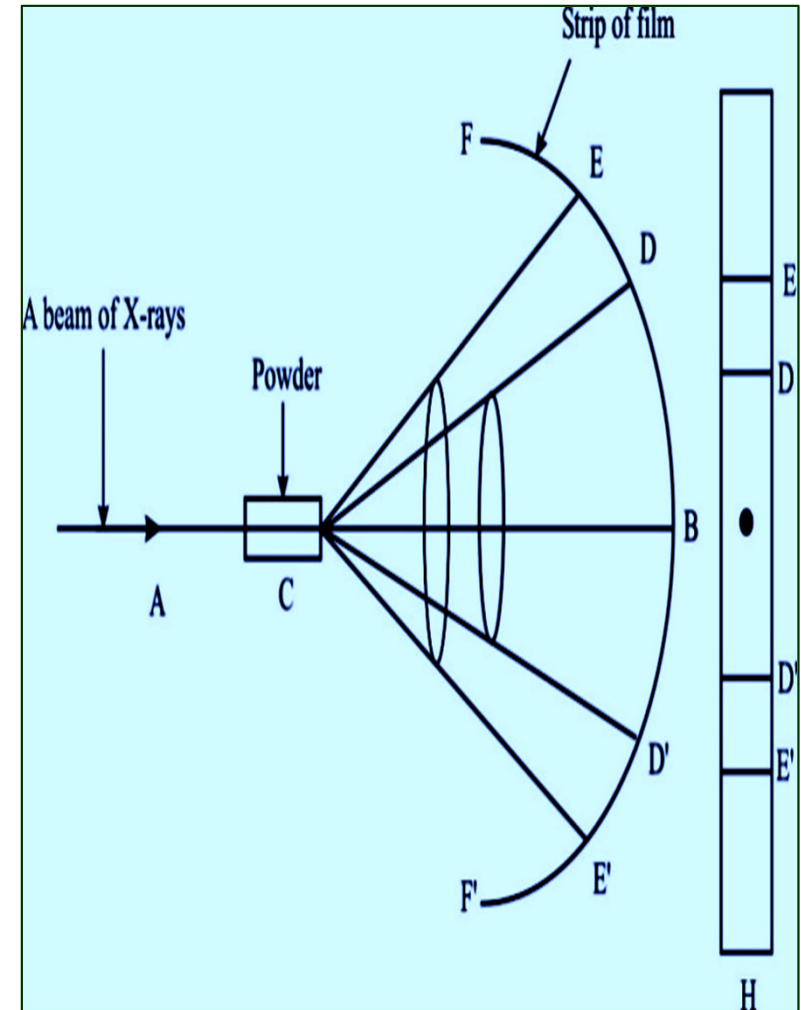
Application of XRD

* XRD is a nondestructive technique
* To identify crystalline phases and orientation
* To determine structural properties: Lattice parameters (10-4Å), strain, grain size, phase composition.
* To measure thickness of thin films and multi-layers
* To determine atomic arrangement

XPS: overview

✓ 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. Siegbahn (Nobel Prize@ 1981@in Physics for developing XPS technique)** and his research group developed the XPS technique.

✓ 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.

✓ The X-Ray source produces photons with certain energies:

  o MgKα photon with an energy of 1253.6 eV

  o 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.
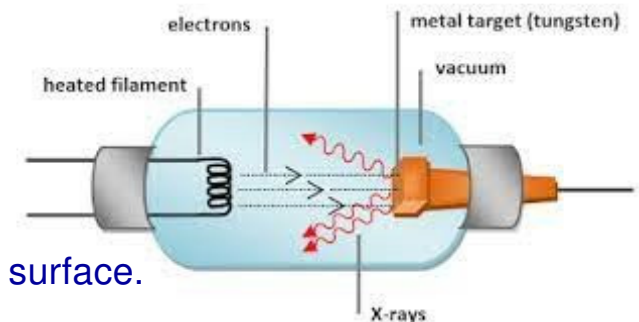
Why the Core Electrons?

✓ 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.

✓ Fermi level is the highest energy level occupied by an electron in a neutral solid at absolute 0 temperature.

✓ Electron binding energy (BE) is calculated with respect to the Fermi level.

✓ The core electrons are local close to the nucleus and have binding energies characteristic of their particular element.

✓ The core electrons have a higher probability of matching the energies of $AlK\alpha$ and $MgK\alpha$.

Valence e⁻

Core e⁻

Atom
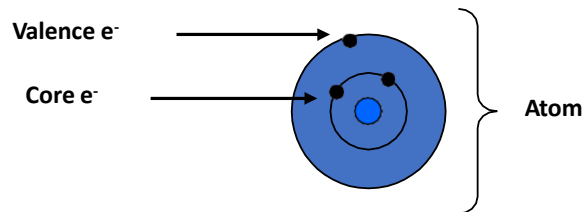
Binding Energy (BE)

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.

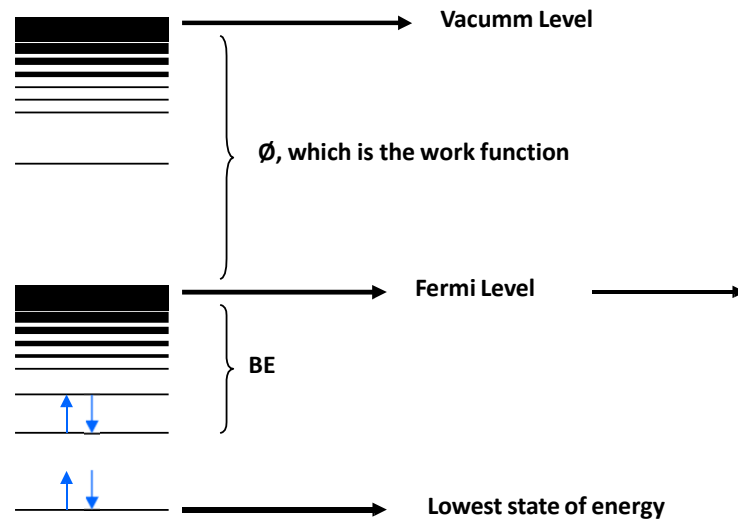**This is the point with 0 energy of attraction between the electron and the nucleus. At this point the electron is free from the atom.**

0

B.E.

x

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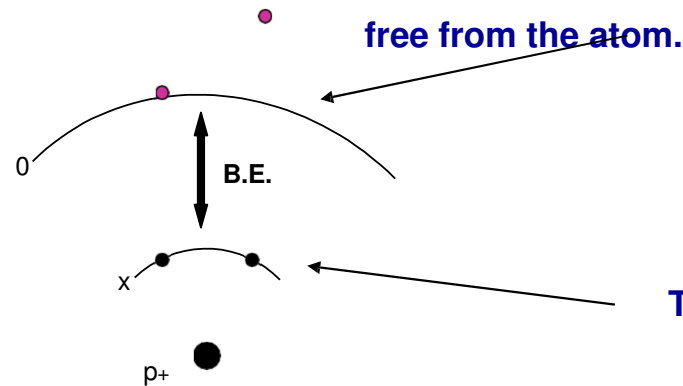
These electrons are attracted to the proton with certain binding energy x

Energy Levels

Vacumm Level

Ø, which is the work function

Fermi Level

At absolute 0 Kelvin the electrons fill from the lowest energy states up.
When the electrons occupy up to this level the neutral solid is in its "ground state."

BE

Lowest state of energy

XPS Instrumentation

Courtesy: David Echevarría Torres @ Univ. of Texas

✓ XPS is also known as ESCA (Electron Spectroscopy for Chemical Analysis).

✓ The technique is widely used because it is very simple to use, and the data is easily analyzed.

✓ XPS works by irradiating atoms of a surface of any solid material with X-Ray photons, causing the ejection of electrons.

University of Texas at El Paso, Physics Department Front view of the Phi 560 XPS/AES/SIMS UHV System
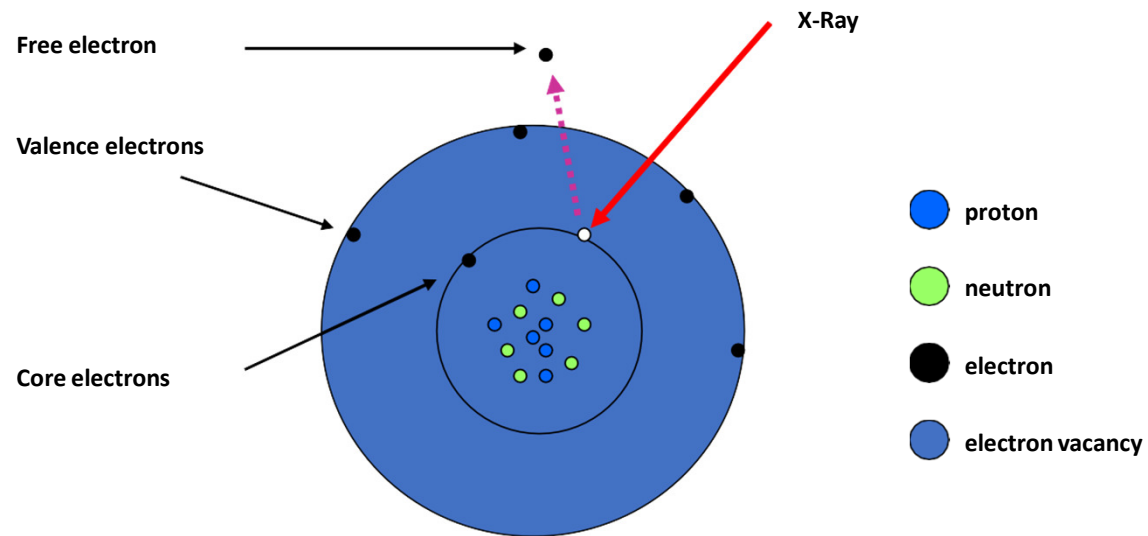
How Does XPS Technology Work?

✓ A monoenergetic x-ray beam emits photoelectrons from the from the surface of the sample.

✓ The X-Rays either of two energies:
  ✓ Al Ka (1486.6eV)
  ✓ Mg Ka (1253.6 eV)

✓ The x-ray photons The penetration 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.

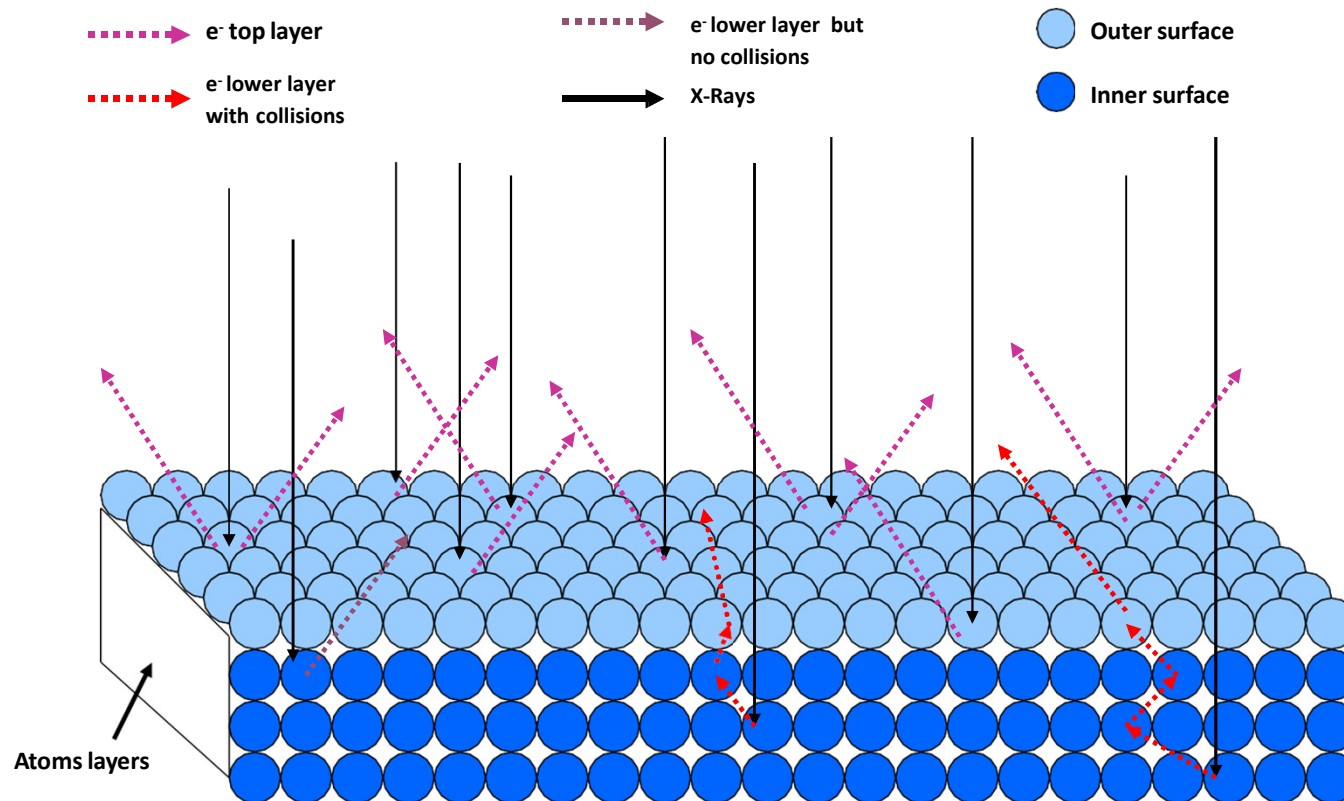Courtesy: David Echevarría Torres @ Univ. of Texas

Importance of UHV in XPS

✓ Contamination of surface

   ✓ **XPS is a surface sensitive technique.**

      ✓ Contaminates will produce an XPS signal and lead to incorrect analysis of the surface of composition.

✓ The pressure of the vacuum system is $\leq 10^{-9}$ Torr

✓ 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.

The Atom and the X-Ray

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

X-Rays on the Surface

e⁻ top layer

e⁻ lower layer but no collisions

Outer surface

e⁻ lower layer with collisions

X-Rays

Inner surface

Atoms layers

Courtesy: David Echevarría Torres @ Univ. of Texas

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 lower in lower energy.

  ✓ They will contribute to the noise signal of the spectrum.

X-Rays and the Electrons

······► Electron without collision

- - -► Electron with collision

X-Ray

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.
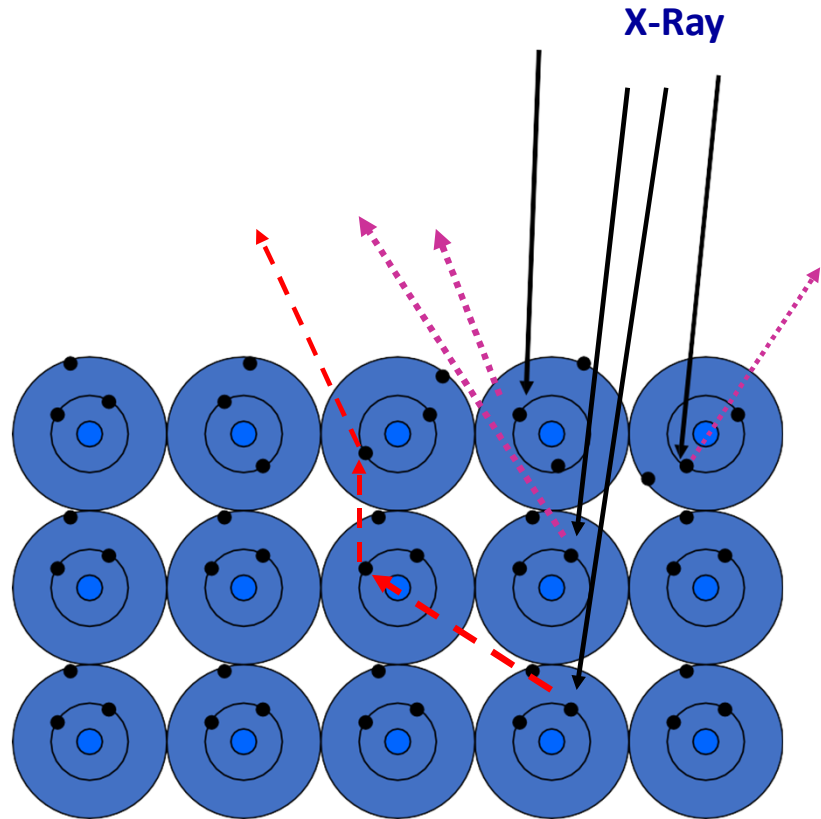
X-Rays and Auger Electrons

✓ When the core electron leaves a vacancy an electron of higher energy will move down to occupy the vacancy while releasing energy by:

    ✓ photons

    ✓ Auger electrons

✓ Each Auger electron carries a characteristic energy that can be measured.

Two Ways to Produce Auger Electrons

1. The X-Ray source can irradiate and remove the e^- from the core level causing the e^- to leave the atom
2. A higher-level e^- will occupy the vacancy.
3. The energy released is given to a third higher level e^-.
4. This is the Auger electron that leaves the atom.

The axial e^- gun can irradiate and remove the core e^- by collision. Once the core vacancy is created, the Auger electron process occurs the same way.

Equation

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

KE → Kinetic Energy (measure in the XPS spectrometer)

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

Ø → spectrometer work function. It is a few eV, it gets more complicated because the materials in the instrument will affect it. Found by calibration.

BE → is the unknown variable

✓The equation will calculate the energy needed to get an e⁻ out from the surface of the solid.

✓Knowing KE, hv and Ø the BE can be calculated.

KE versus BE

# of electrons

Binding energy

(eV)

E   E   E
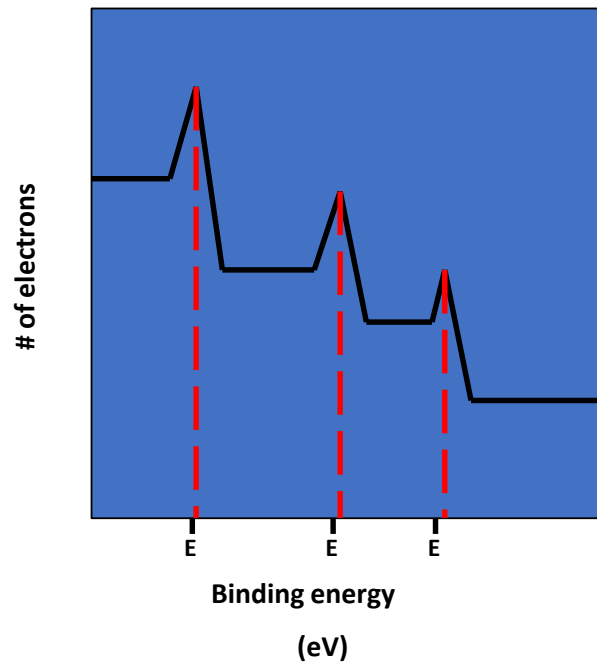
KE can be plotted depending on BE

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

Courtesy: David Echevarría Torres @ Univ. of Texas

Interpreting XPS Spectrum: Background

✓ **The X-Ray will hit the e-s in the bulk (inner e- layers) of the sample**

✓ **e- will collide with other e- from top layers, decreasing its energy to contribute to the noise, at lower kinetic energy than the peak .**

✓ **The background noise increases with BE because the SUM of all noise is taken from the beginning of the analysis.**

$N_{tot} = N_1 + N_2 + N_3 + N_4$
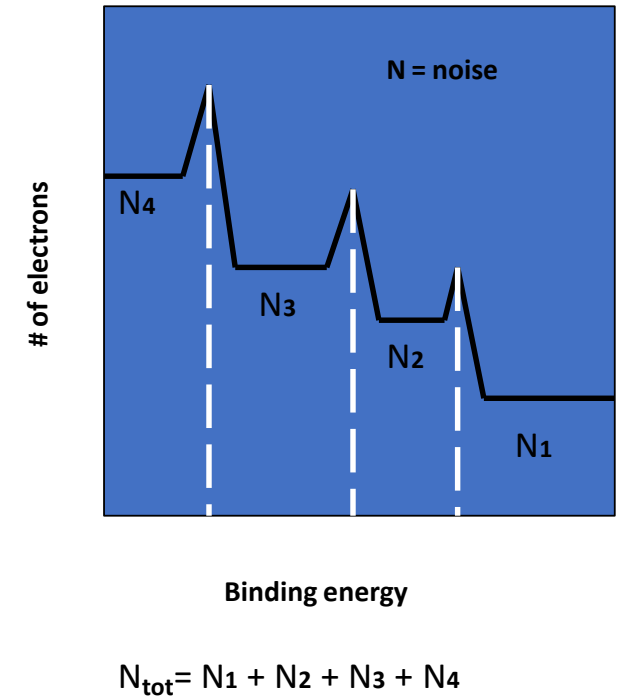
XPS Spectrum
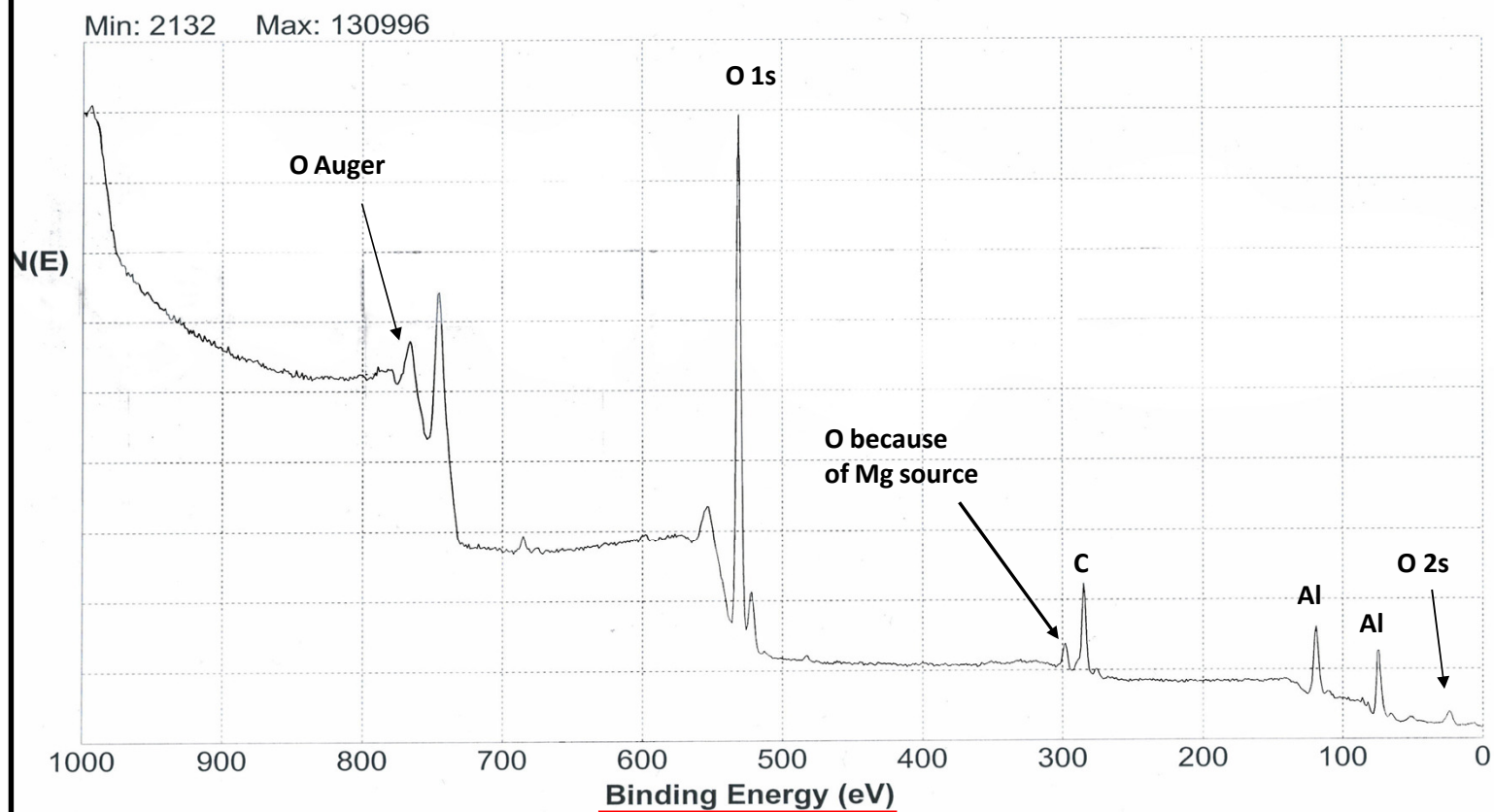
✓ The XPS peaks are sharp.

✓ In a XPS graph it is possible to see Auger electron peaks.

✓ The Auger peaks are usually wider peaks in a XPS spectrum.

✓ Aluminum foil is used as an example on the next slide.

AES Survey

C:\PHYS 3243\AES Survey Demo Al foil with carbon contamination.ASN
Acquired: Thursday, November 30, 2006 13:43:46

EV/Step: 1 eV,   Time/Step: 25 mSec,   Sweeps: 10,   Beam: 3000 V,   Input: VF1

Min: 211590   Max: 487593

Auger Spectrum

N(E)

**Characteristic of Auger graphs
The graph goes up as KE increases.**

40   186   332   478   624   770   916   1062   1208   1354   1500
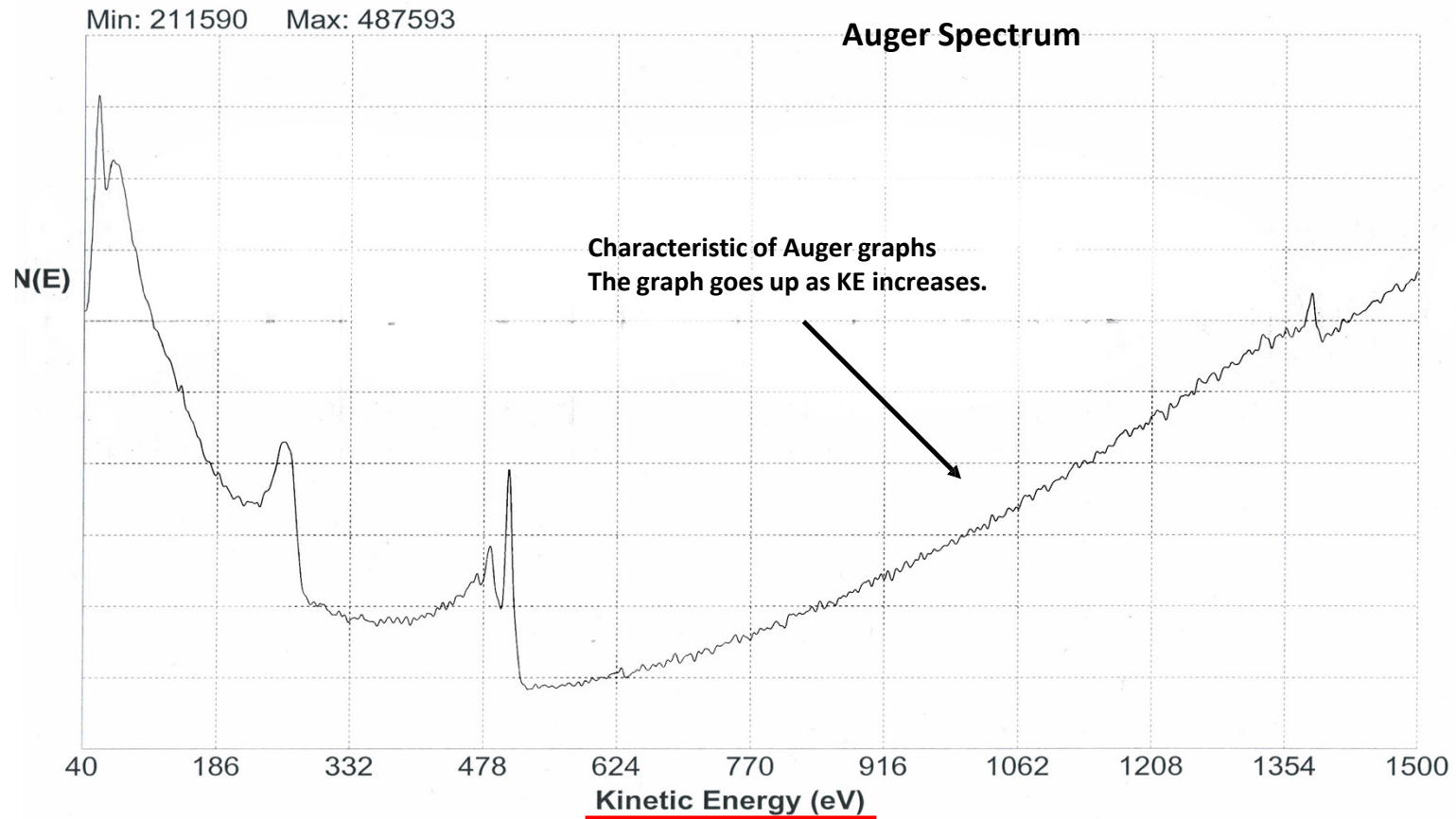
Kinetic Energy (eV)

Courtesy: David Echevarría Torres @ Univ. of Texas

**Sample and graphic provided by William Durrer, Ph.D.
Department of Physics at the Univertsity of Texas at El Paso**

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.

X-rays vs e⁻ Beam

✓ **X-Rays**

  ✓ Hit all sample area simultaneously permitting data acquisition that will give an
     idea of the average composition of the whole surface.

✓ **Electron Beam**

  ✓ It can be focused on a particular area of the sample to determine the
     composition of selected areas of the sample surface.

XPS Technology

✓ Consider 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