

X-RAY PHOTO ELECTRON SPECTROSCOPY (XPS)

X-ray photoelectron spectroscopy (XPS) is a surface characterization technique that can analyze a sample to a depth of 2 to 5 nanometers.

XPS reveals the chemical elements that are present at the surface and the nature of the chemical bond that exists between these elements. It can detect all elements except hydrogen and helium.

Principle

When an X-ray bombards a sample, some electrons become excited and escape to the surface of the atom. The other electrons undergo emission and suffer no energy loss in escaping the surface and into the surrounding vacuum. Once these photo ejected electrons are in the vacuum, they are collected by an electron analyzer that measures their kinetic energy.

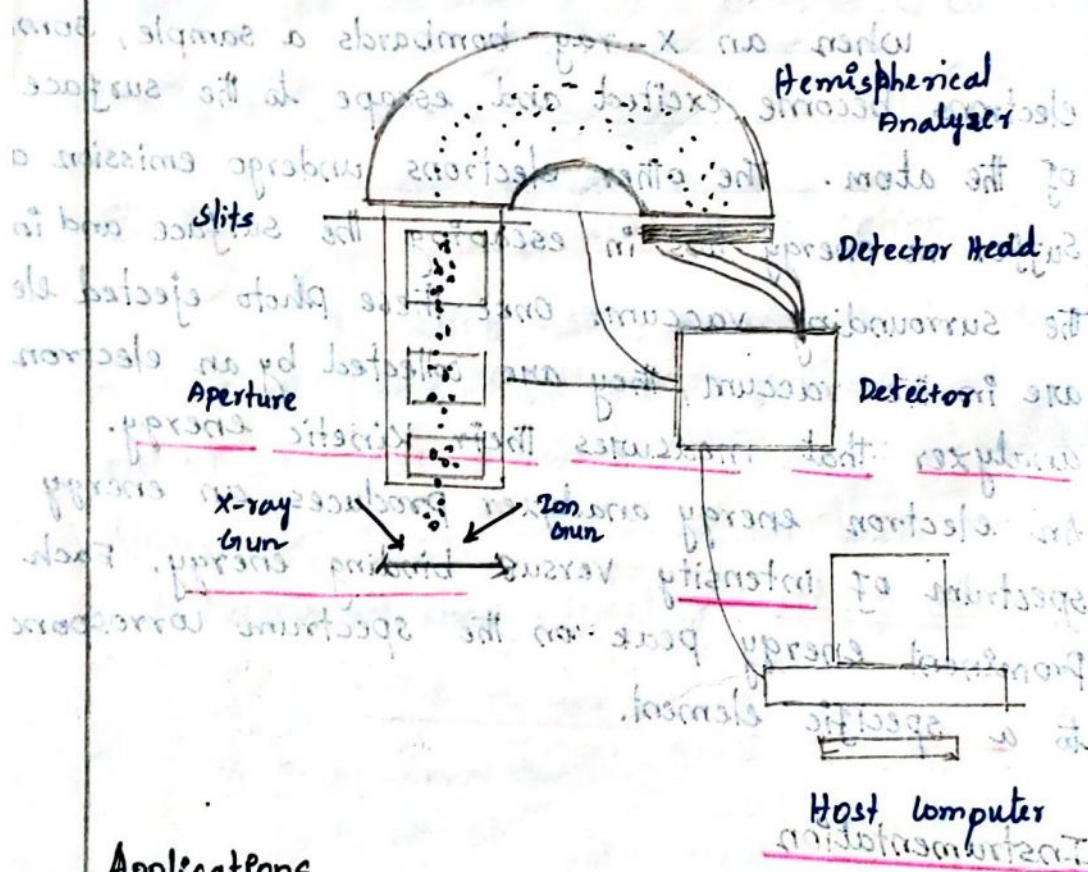
An electron energy analyzer produces an energy spectrum of intensity versus binding energy. Each prominent energy peak on the spectrum corresponds to a specific element.

Instrumentation

XPS is conducted in ultrahigh vacuum (UHV) conditions, around 10^{-9} millibar. Atmospheric pressure is about 1 bar, which means that the number of atoms of gas in a UHV chamber is one-trillionth that of air per unit of volume.

When X-rays are illuminated through

the sample under study, it causes the ejection of electrons having different range of energies and directions. These emitted electrons are collected by set of electrostatic and or magnetic lens units and transferred through the apertures and focused onto the analyzer entrance slit. Electrostatic fields within the hemispherical analyzer (HSA) are established in such a way that it allows electrons of a given energy to arrive at the detector slits and onto the detectors for recording.



Applications

1. XPS is used for the surface analysis of organic and inorganic materials.
2. It is used to study the surface analysis of copper.
3. It is used to study the fibre glass surfaces.
4. It is used to study the film oxide thickness measurement.
5. It is a unique approach in probing electronic structure.

MILLER INDICES

Various planes of a crystal are to be characterized and indexed for a better understanding of the crystal

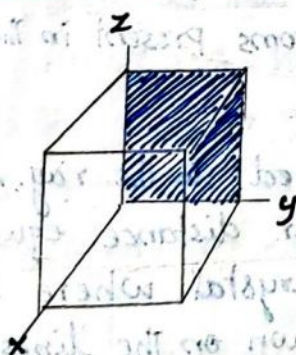
Miller introduced a set of integers (hkl) to specify a plane of the crystal. This set of three numbers (hkl) is known as Miller indices of a particular plane of a crystal.

The Miller indices (hkl) of a plane of a crystal are inversely proportional to the intercepts of that plane on the three crystallographic axes.

Rules for Miller Indices

1. Find the intercepts on the x , y and z axes.
2. Specify the intercepts in fractional coordinates.
3. Take the reciprocals of the fractional intercepts.
4. Using an appropriate multiplier, convert the $1/\text{intercept}$ set to the smallest possible set of whole numbers
5. Represent the above as a set of integers (hkl) for a given plane of a crystal.

Examples



Plane is parallel to z axis (∞)

1. Intercepts

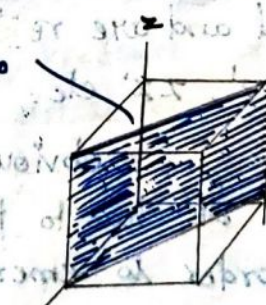
$$x=1, y=a, z=\infty$$

2. Reciprocals

$$\frac{1}{1}, \frac{1}{a}, \frac{1}{\infty}$$

3. Miller indices

$$(1 \ 0 \ 0)$$



Plane is on the y axis (1)

1. Intercepts

$$x=1, y=1, z=\infty$$

2. Reciprocals

$$\frac{1}{1}, \frac{1}{1}, \frac{1}{\infty}$$

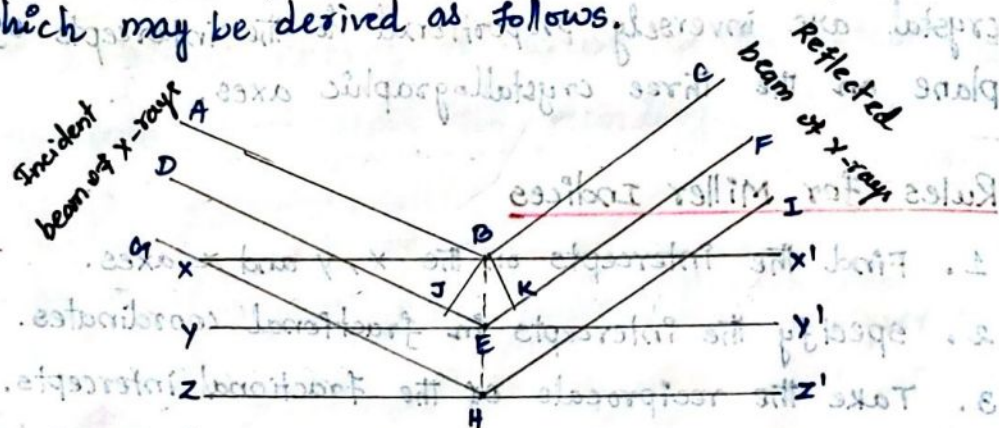
3. Miller indices

$$(1 \ 1 \ 0)$$

INVESTIGATION OF INTERNAL STRUCTURE OF A SOLID BY X-RAY DIFFRACTION - BRAGG'S LAW

Bragg devised a spectrometer for the measurements of intensity of x-ray beams. The diffraction pattern thus obtained is used to study the crystal structure.

The Bragg's method for the study of the internal structure of crystal is based upon the Bragg's equation, which may be derived as follows.



A crystal may be considered to be made up of a parallel equidistant atomic planes as represented by the lines xx' , yy' , zz' etc. Suppose a beam of x-rays is incident on the crystal at an angle θ , a part of the beam, say for example the ray AB is reflected at the point B along the path BC . On the other hand some rays like DE , GH etc., penetrate into the crystal and are reflected by the atoms present in the atomic planes yy' , zz' etc.

Obviously, as compared to the ray AB , a ray like DE has to travel a longer distance equal to JEK in order to emerge out of the crystal where BJ and BK are the perpendiculars drawn on the lines DE and EF respectively.

If a photographic plate is placed to receive the reflected rays, a diffraction pattern is obtained.

Since the reflected rays BC and EF are in phase the extra distance JEK traversed by the ray DE

Should be an integral multiple of the wavelength λ of the x-rays

i.e. Distance $JEK = n\lambda \rightarrow \textcircled{1}$

where n is an integer i.e. 1, 2, 3, 4 etc. If d is the distance between the successive atomic phases it is obvious from the figure that

$$JE = EK - d \sin \theta$$

$$\left[\because \sin \theta = \frac{JE}{BE} = \frac{JE}{d} \right]$$

$$JEK = 2d \sin \theta$$

So that putting the value in equ (1) we get

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

This equation is called Bragg's equation.

Critical constants

Critical temperature (T_c)

Critical temperature (T_c) of a gas may be defined as that temperature above which the gas cannot be liquefied, however, high pressure we may apply on the gas. For example the critical temperature of CO_2 is 31.1°C . This means that it is not possible to liquefy CO_2 above 31.1°C by any means.

Critical pressure (P_c)

The minimum pressure required to liquefy the gas at the critical temperature is called the critical pressure (P_c). For example, at 31.1°C , carbon dioxide can be liquefied under a pressure of 72.9 atm. Thus the critical pressure of CO_2 is 72.9 atm.