X-Ray Spectroscopy

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Introduction

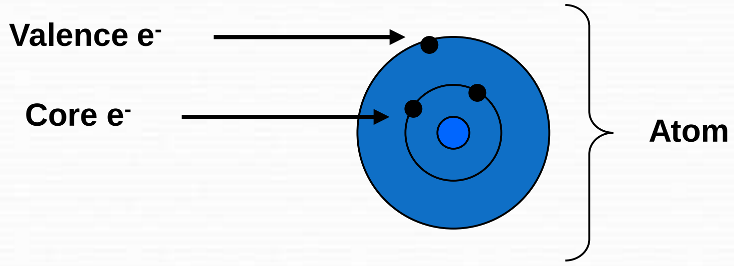
- X-ray spectroscopy is based on the measurement of emission, absorption, scattering, fluorescence and diffraction of EMR
- X-rays are short wavelength EMR produced by the deceleration of high energy electrons or by electronic transition of electrons in the inner orbitals of atoms.
- The wavelength range of X-rays is from about 10^{-5} A^0 to 100 A^0. conventional spectroscopy confined to the region of about 0.1 A^0 to 25 A^0. i.e. 0.01 nm to 2.5 nm (1 A^0 = 0.1 nm)

Method of X-ray analysis

1) X-ray Emission Spectroscopy (XES)
2) Auger Emission Spectroscopy (AES)
3) X-ray Fluorescence Spectroscopy (XFS)
4) Electron Spectroscopy for Chemical Analysis (ESCA)
5) X-ray Absorption Spectroscopy (XAS)
6) X-ray Diffraction Spectroscopy (XRDS)

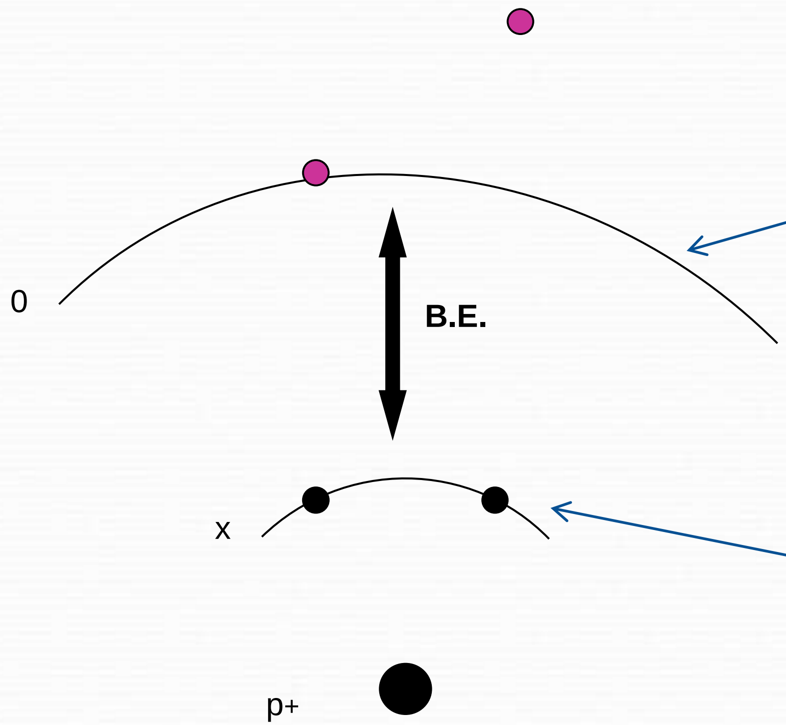
Why the Core Electrons?

- 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 e^-s are local close to the nucleus and have binding energies characteristic of their particular element.
- The core e^-s have a higher probability of matching the energies of AlKα and MgKα.



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**

X-ray Emission Spectroscopy (XES)

- When atom is excited by removal of an electron from inner level, it relax by transfering an electron from some outer level to the vacant inner level with emission of X-ray photon.

- If X-rays emitted, their

  λ ……charecteristic of element

  Intensity α no. of excited atoms

- Here the atom is excited by applying primary electron beam which ejects electron from inner energy level

Auger Emission Spectroscopy (AES)

- 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.

X-ray Fluorescence Spectroscopy (XFS)

- Atoms are excited by irradiation of the material with X-rays of shorter wavelength (higher energy)

- The primary beam of X-rays ejects electrons from inner energy level. Then X-rays are emitted as electrons from outer levels to vacant inner level

Electron Spectroscopy for Chemical Analysis (ESCA)

- Primary X-rays eject electrons from inner energy levels, the energy of the emitted electrons are measured

X-ray Absorption Spectroscopy (XAS)

- A beam of X-ray is allowed to pass through the sample, and the fraction or attenuation of X-ray photons absorbed is considered to be a measure of the concentration of absorbing substance.

X-ray Diffraction Spectroscopy (XRDS)

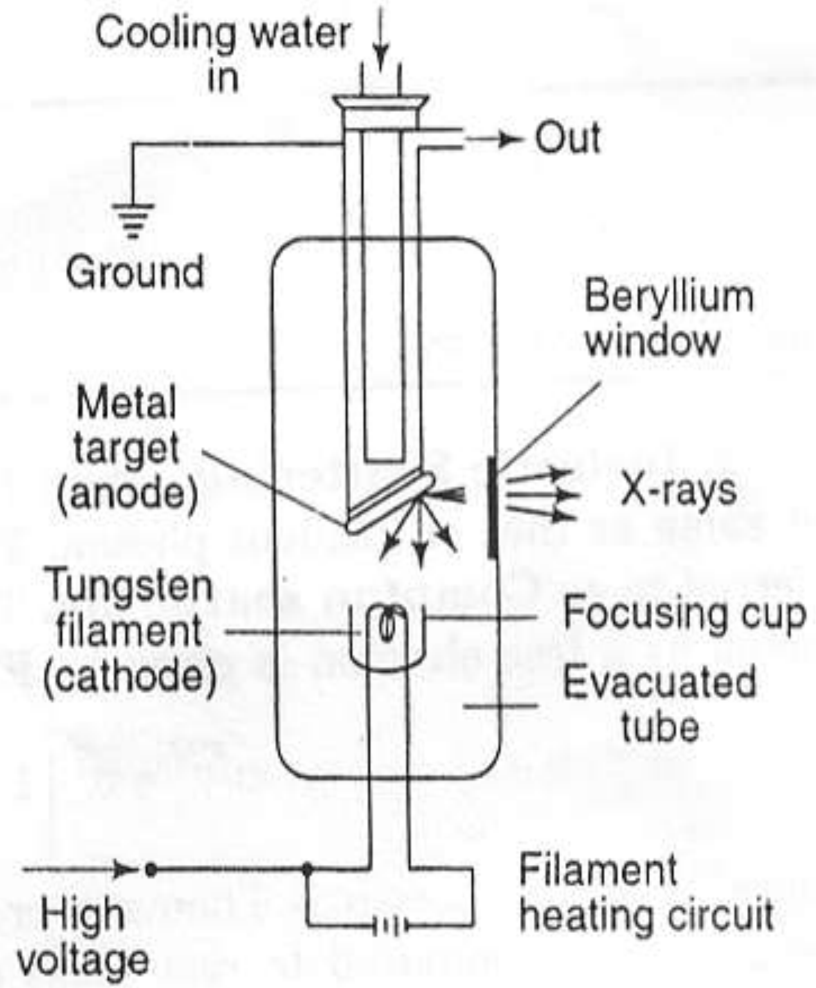
- Diffraction of X-rays from the planes of crystal is observed when a beam of X-rays is allowed to pass through crystal

- This method depends on the wave character of the X-rays and the regular spacing of planes in a crystal

Generation of X- rays

- for analytical purposes, X-rays are obtained in four ways…

1. By bombardment of a metal target with a beam of higher energy electron.
2. By exposure of a substance to a primary beam of X-rays inorder to to generate a secondary beam of X-ray fluorescence.
3. By use of a radioactive source whose decay results in X-ray emission
4. From a synchrotron radiation source



coolidge tube.

Spectra from different sources

- Electron beam sources produce
  - Continuum spectra
  - Line spectra
- Fluorescent source produce
  - line spectra
- radioactive source produces
  - line spectra

X-ray Diffraction (XRD)

A. When X-rays interact with a single particle, it scatters the incident beam uniformly in all directions.

B. When X-rays interact with a solid material the scattered beams can add together in a few directions and reinforce each other to yield diffraction. The regularity of the material is responsible for the diffraction of the beams.

For example if you look at a CD when exposed to white light you can see it diffracted into varies wavelengths of color. The pits (or grooves) in the CD are the regularity of the material that causes the diffraction.

- Diffraction can occur when any electromagnetic radiation interacts with a periodic structure. The repeat distance of the periodic structure must be about the same wavelength of the radiation. For example, light can be diffracted by a grating having scribed lines arranged on the order of the wavelength of light.
- X-rays have wavelengths on the order of a few angstroms (1 Angstrom = 0.1 nm). This is the typical inter-atomic distance in crystalline solids, making X-rays the correct order of magnitude for diffraction of atoms of crystalline materials.

How are Diffractions Patterns Made?

When X-rays are scattered from a crystalline solid they can constructively interfere, producing a diffracted beam. What does this mean?

Constructive vs. Destructive Interference

Interference occurs among the waves scattered by the atoms when crystalline solids are exposed to X-rays. There are two types of interference depending on how the waves overlap one another.

- Constructive interference occurs when the waves are moving in phase with each other. Destructive interference occurs when the waves are out of phase.

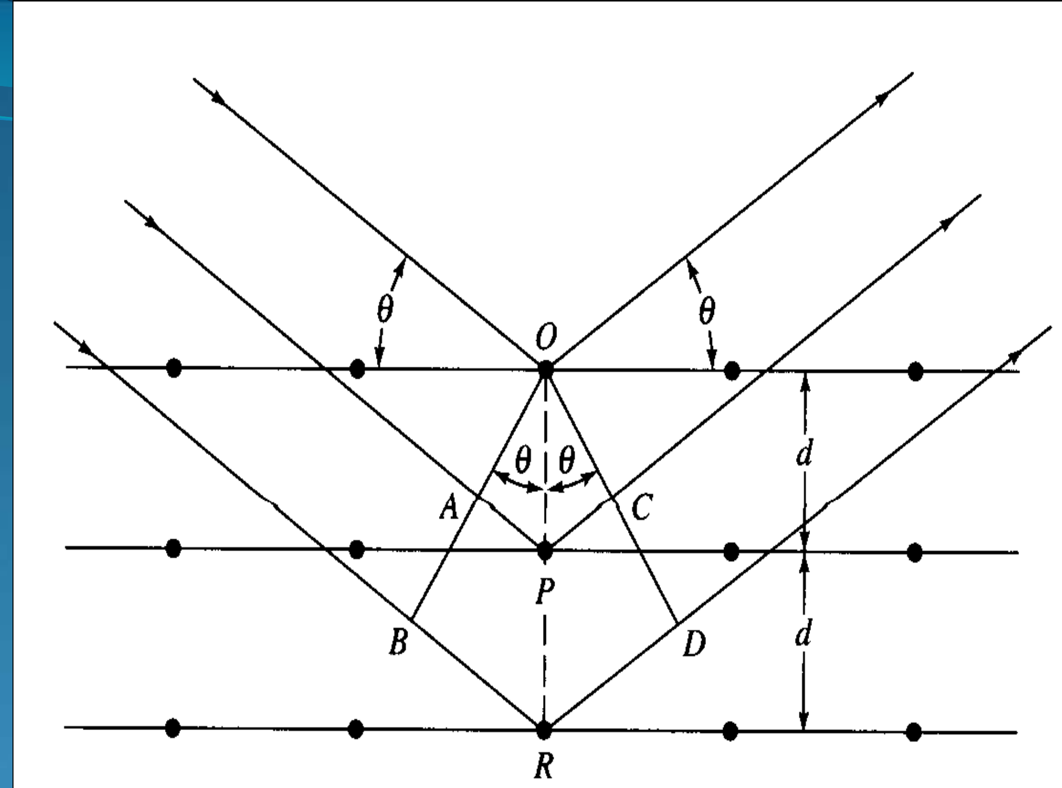
This constructive interference results in diffraction patterns.

$$AP + PC = n\lambda$$

$$AP = PC = d\sin\theta$$

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

$$\sin\theta = \frac{n\lambda}{2d}$$



Constructive interference only at angles proportional to l and d!

If l is known and q can be measured then you can calculate d!

If d is known and q can be measured then you can calculate l!

Debye-Scherrer Powder Diffractometer (Camera)