X-RAY DIFFRACTION METHODS

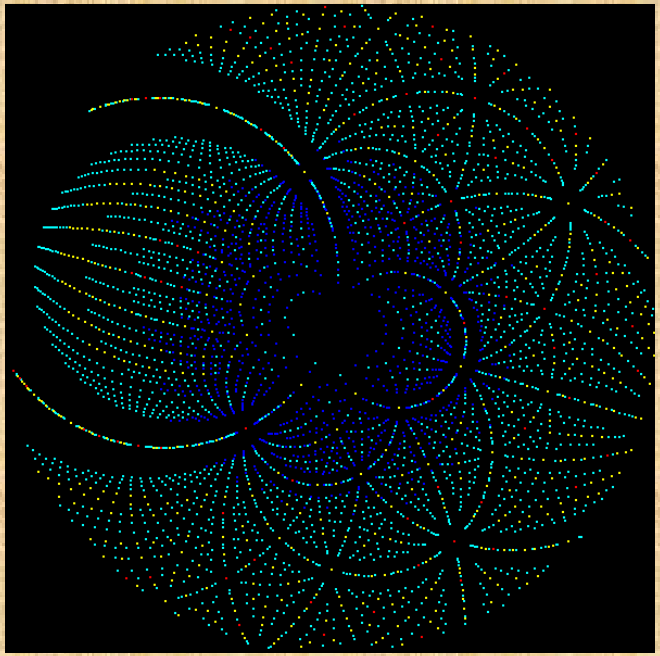
X-Ray Diffraction Method

Laue	Rotating Crystal	Powder
Orientation Single Crystal Polychromatic Beam Fixed Angle	Lattice constant Single Crystal Monochromatic Beam Variable Angle	Lattice Parameters Polycrystal (powdered) Monochromatic Beam Variable Angle

LAUE METHOD

- The Laue method is mainly used to determine the orientation of large single crystals while radiation is reflected from, or transmitted through a fixed crystal.

- The diffracted beams form arrays of spots, that lie on curves on the film.

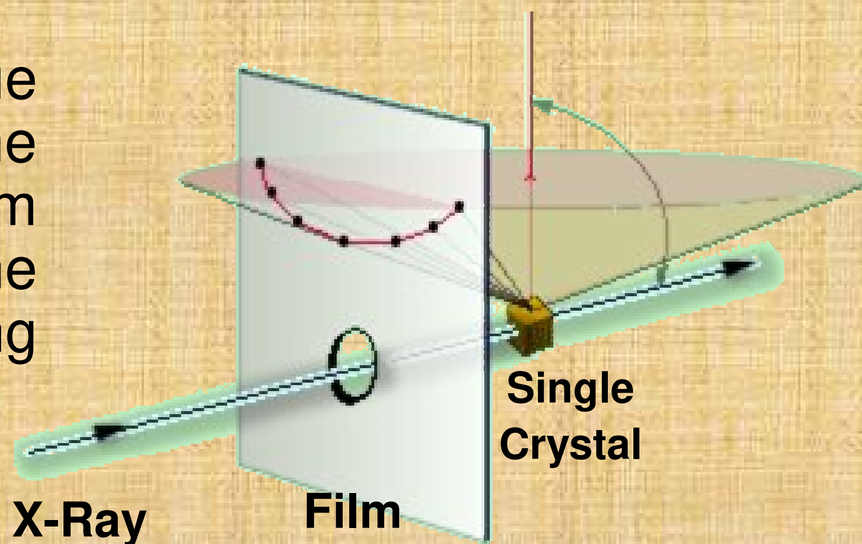


- The Bragg angle is fixed for every set of planes in the crystal. Each set of planes picks out and diffracts the particular wavelength from the white radiation that satisfies the Bragg law for the values of *d* and θ involved.

Back-reflection Laue Method

- In the back-reflection method, the film is placed **between** the x-ray source and the crystal. The beams which are diffracted in a backward direction are recorded.

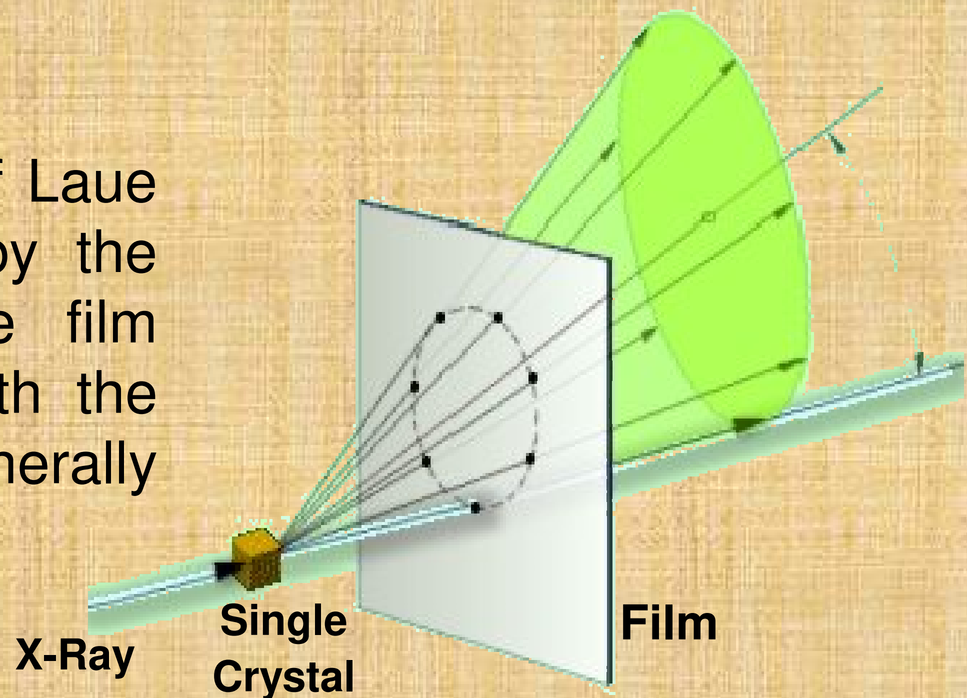
- One side of the cone of Laue reflections is defined by the transmitted beam. The film intersects the cone, with the diffraction spots generally lying on an hyperbola.



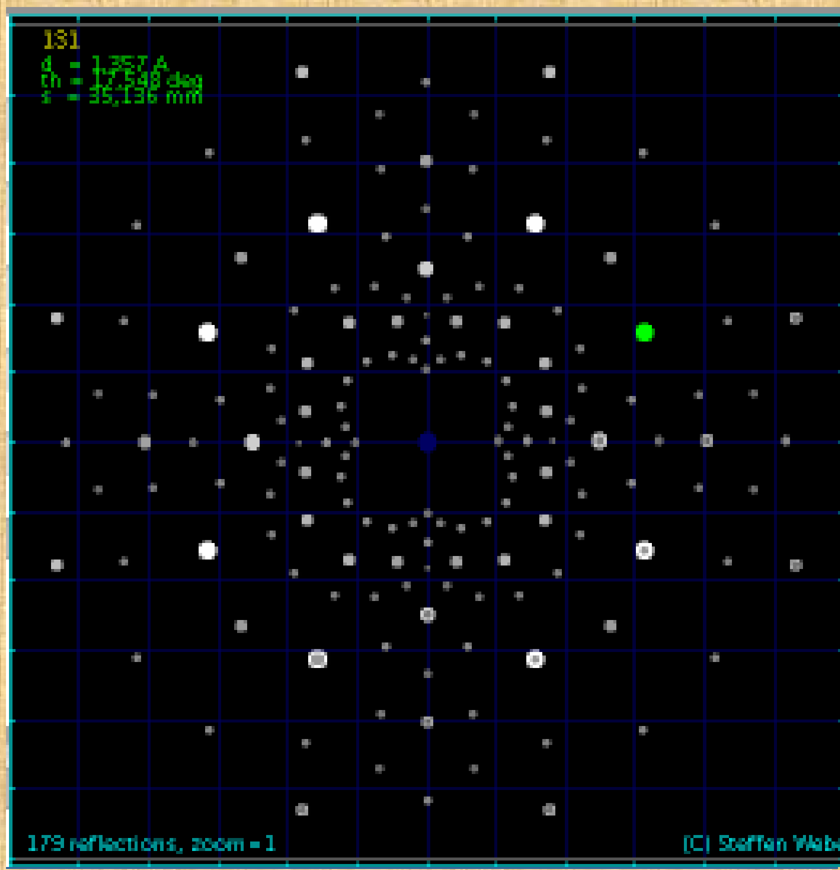
Transmission Laue Method

- In the transmission Laue method, the film is placed **behind** the crystal to record beams which are transmitted through the crystal.

- One side of the cone of Laue reflections is defined by the transmitted beam. The film intersects the cone, with the diffraction spots generally lying on an ellipse.



Laue Pattern



The symmetry of the spot pattern reflects the symmetry of the crystal when viewed along the direction of the incident beam. Laue method is often used to determine the orientation of single crystals by means of illuminating the crystal with a continuos spectrum of X-rays;

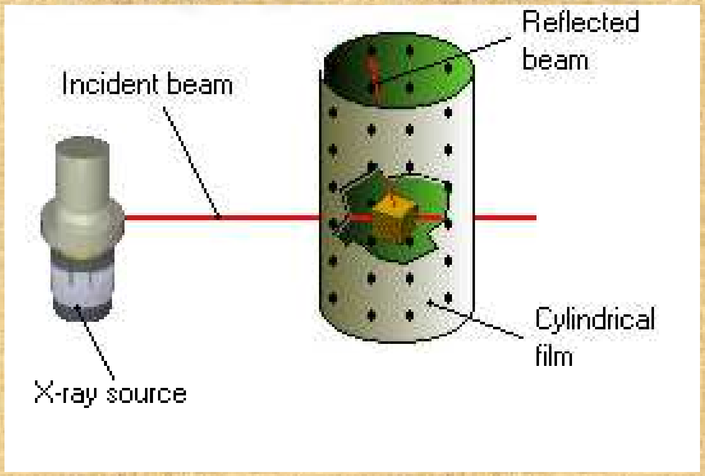
- ☑ ***Single crystal***
- ☑ ***Continous spectrum of x-rays***
- ☑ ***Symmetry of the crystal; orientation***

Crystal structure determination by Laue method

- Therefore, the Laue method is mainly used to determine the crystal orientation.
- Although the Laue method can also be used to determine the crystal structure, several wavelengths can reflect in different orders from the same set of planes, with the different order reflections superimposed on the same spot in the film. This makes crystal structure determination by spot intensity diffucult.
- Rotating crystal method overcomes this problem. How?

ROTATING CRYSTAL METHOD

- In the rotating crystal method, a single crystal is mounted with an axis normal to a monochromatic x-ray beam. A cylindrical film is placed around it and the crystal is rotated about the chosen axis.



- As the crystal rotates, sets of lattice planes will at some point make the correct Bragg angle for the monochromatic incident beam, and at that point a diffracted beam will be formed.

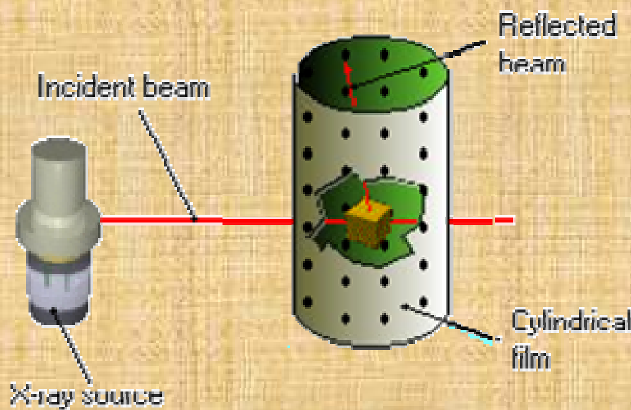
ROTATING CRYSTAL METHOD

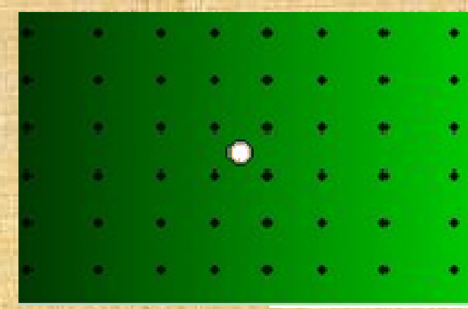
Lattice constant of the crystal can be determined by means of this method; for a given wavelength if the angle θ at which a reflection occurs is known, d_{hkl} can be determined.

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Rotating Crystal Method

The reflected beams are located on the surface of imaginary cones. By recording the diffraction patterns (both angles and intensities) for various crystal orientations, one can determine the shape and size of unit cell as well as arrangement of atoms inside the cell.





Film

THE POWDER METHOD

If a powdered specimen is used, instead of a single crystal, then there is ***no need to rotate*** the specimen, because there will always be some crystals at an orientation for which diffraction is permitted. Here a monochromatic X-ray beam is incident on a powdered or polycrystalline sample.

This method is useful for samples that are difficult to obtain in single crystal form.

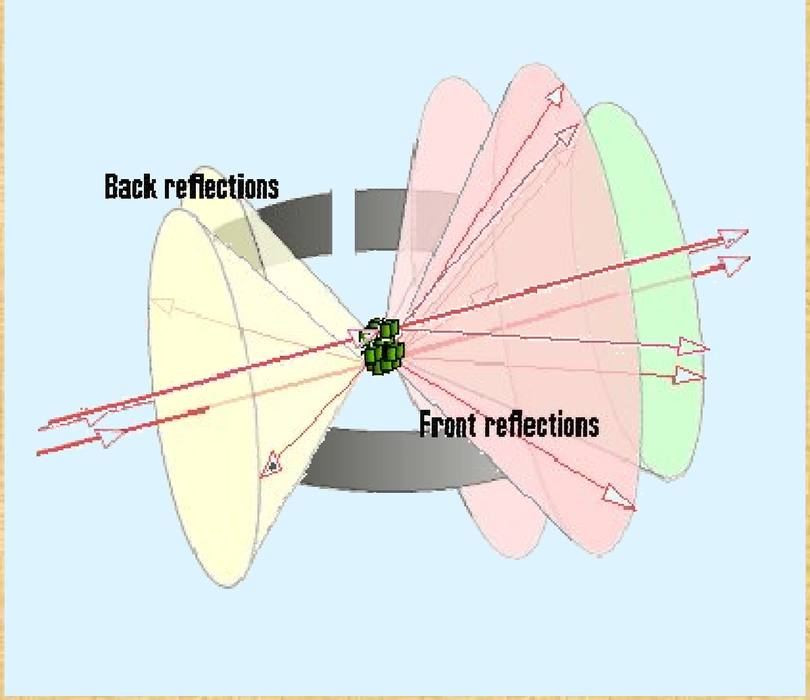
THE POWDER METHOD

The powder method is used to determine the value of the lattice parameters accurately. Lattice parameters are the magnitudes of the unit vectors **a**, **b** and **c** which define the unit cell for the crystal.

For every set of crystal planes, by chance, ***one or more crystals*** will be in the ***correct orientation*** to give the correct Bragg angle to satisfy Bragg's equation. Every crystal plane is thus capable of diffraction. Each diffraction line is made up of a large number of small spots, each from a separate crystal. Each spot is so small as to give the appearance of a continuous line.

The Powder Method

- If a monochromatic x-ray beam is directed at a single crystal, then only one or two diffracted beams may result.



The Powder Method

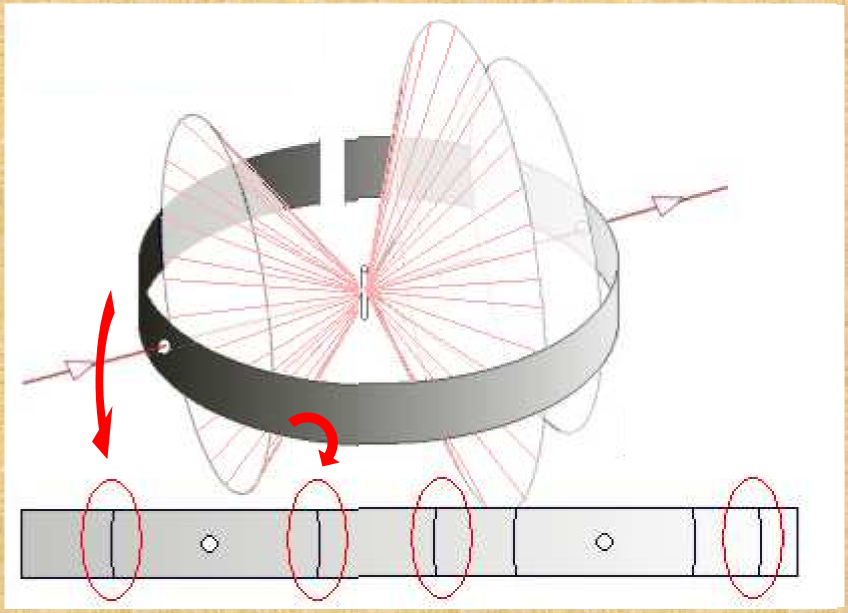
- If the sample consists of some tens of randomly orientated single crystals, the diffracted beams are seen to lie on the surface of several cones. The cones may emerge in all directions, forwards and backwards.

- A sample of some hundreds of crystals (i.e. a powdered sample) show that the diffracted beams form continuous cones. A circle of film is used to record the diffraction pattern as shown. Each cone intersects the film giving diffraction lines. The lines are seen as arcs on the film.

Debye Scherrer Camera

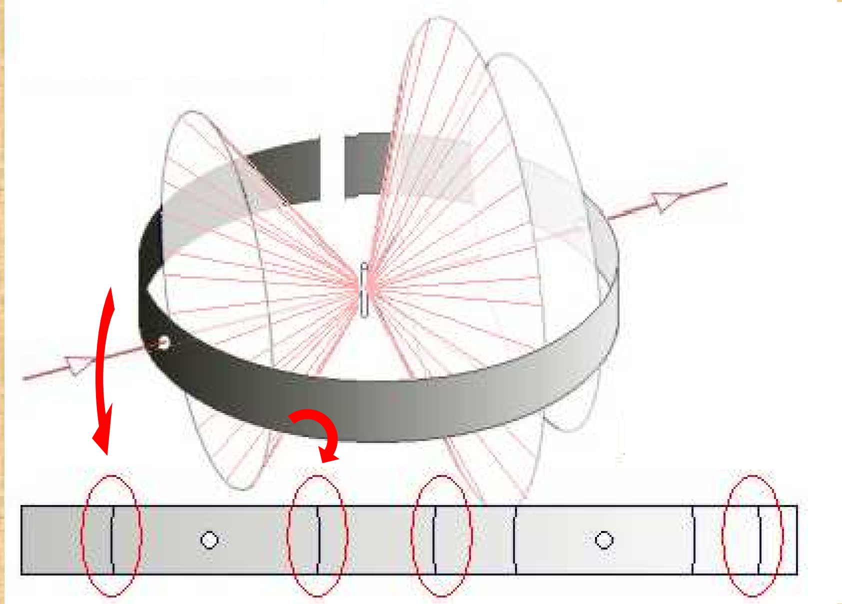
A very small amount of powdered material is sealed into a fine capillary tube made from glass that does not diffract x-rays.

The specimen is placed in the **Debye Scherrer** camera and is accurately aligned to be in the centre of the camera. X-rays enter the camera through a collimator.



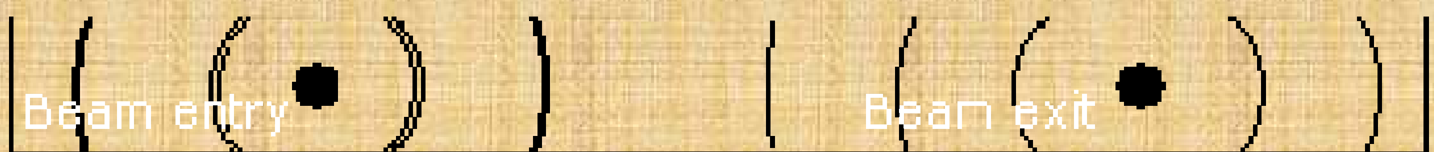
Debye Scherrer Camera

The powder diffracts the x-rays in accordance with Braggs law to produce cones of diffracted beams. These cones intersect a strip of photographic film located in the cylindrical camera to produce a characteristic set of arcs on the film.



Powder diffraction film

When the film is removed from the camera, flattened and processed, it shows the diffraction lines and the holes for the incident and transmitted beams.



Application of XRD

XRD is a nondestructive technique. Some of the uses of x-ray diffraction are;

1. Differentiation between crystalline and amorphous materials;
2. Determination of the structure of crystalline materials;
3. Determination of electron distribution within the atoms, and throughout the unit cell;
4. Determination of the orientation of single crystals;
5. Determination of the texture of polygrained materials;
6. Measurement of strain and small grain size…..etc

Advantages and disadvantages of X-rays

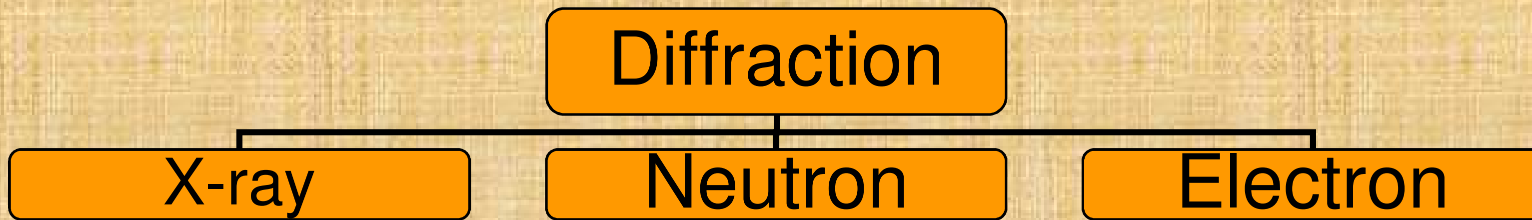
<u>Advantages;</u>

- X-ray is the cheapest, the most convenient and widely used method.
- X-rays are not absorbed very much by air, so the specimen need not be in an evacuated chamber.

<u>Disadvantage;</u>

- They do not interact very strongly with lighter elements.

Difraction Methods



Different radiation source of neutron or electron can also be used in diffraction experiments.

The physical basis for the diffraction of electron and neutron beams is the same as that for the diffraction of X rays, the only difference being in the mechanism of scattering.

Neutron Diffraction

- Neutrons were discovered in 1932 and their wave properties was shown in 1936.

$$E = p^2/2m \quad p = h/\lambda$$

E=Energy λ=Wavelength
p=Momentum
m_n=Mass of neutron = 1,67.10^{-27}kg

- λ ~1A°; Energy E~0.08 eV. This energy is of the same order of magnitude as the thermal energy kT at room temperature, 0.025 eV, and for this reason we speak of thermal neutrons.

Neutron Diffraction

- Neutron does not interact with electrons in the crystal. Thus, unlike the x-ray, which is scattered entirely by electrons, the neutron is scattered entirely by nuclei
- Although uncharged, neutron has an intrinsic magnetic moment, so it will interact strongly with atoms and ions in the crystal which also have magnetic moments.
- Neutrons are more useful than X-rays for determining the crystal structures of solids containing light elements.
- Neutron sources in the world are limited so neutron diffraction is a very special tool.

Neutron Diffraction

Neutron diffraction has several advantages over its x-ray counterpart;

- Neutron diffraction is an important tool in the investigation of magnetic ordering that occur in some materials.

- Light atoms such as H are better resolved in a neutron pattern because, having only a few electrons to scatter the X ray beam, they do not contribute significantly to the X ray diffracted pattern.

Electron Diffraction

Electron diffraction has also been used in the analysis of crystal structure. The electron, like the neutron, possesses wave properties;

$$E = \frac{\hbar^2 k^2}{2m_e} = \frac{h^2}{2m_e \lambda^2} = 40eV \qquad \lambda \approx 2A^0$$

Electrons are ***charged particles*** and interact strongly with all atoms. So electrons with an energy of a few eV would be completely ***absorbed by the specimen***. In order that an electron beam can penetrate into a specimen , it necessitas a beam of very high energy (50 keV to 1MeV) as well as the specimen must be thin (100-1000 nm)

Electron Diffraction

If low electron energies are used, the penetration depth will be very small (only about 50 A°), and the beam will be reflected from the surface. Consequently, electron diffraction is a useful technique for surface structure studies.

Electrons are scattered strongly in air, so diffraction experiment must be carried out in a high vacuum. This brings complication and it is expensive as well.

Diffraction Methods

X-Ray	Neutron	Electron
λ = 1A°	λ = 1A°	λ = 2A°
E ~ 10^4 eV	E ~ 0.08 eV	E ~ 150 eV
interact with electron Penetrating	interact with nuclei Highly Penetrating	interact with electron Less Penetrating