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CONDENSED MATTER PHYSICS

(NET/JRF, GATE, JEST, TIFR)

Condensed Matter Physics

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CHAPTER-2
X-RAY DIFFRACTION

X-ray diffraction is a method of determining the structure of a crystal from its diffraction pattern. X-ray diffraction techniques are based on the elastic scattering of x-rays from structures that have long range order. The extensive use of X-rays for the analysis of atomic structural arrangements is based on the fact that waves undergo a phenomenon called diffraction when interacting with systems (diffracting centers) which are spaced at distances of the same order of magnitude as the wavelength of the particular radiation considered. X-ray diffraction in crystalline solids takes place because the atomic spacings are in the 10^{-10}m range, as are the wavelengths of X-rays. Since there is no convenient way to focus X-rays with lenses and to magnify images, we do not attempt to look directly at atoms. Rather, we consider the interference effects of X-rays when scattered by the atoms, comprising a crystal lattice. This is analogous to studying the structure of an optical diffraction grating by examining the interference pattern produced when we shine visible light on the grating. (The spacing of lines on a grating is about 0.5 to 1 μm and the wavelength of visible radiation ranges from 0.4 to 0.8 μm.) In the optical grating the ruled lines act as scattering centers, whereas in a crystal it is the atoms (more correctly, the electrons about the atom) which scatter the incident radiation. In the following section we will study the theory of the x-ray diffraction from a crystalline solid.

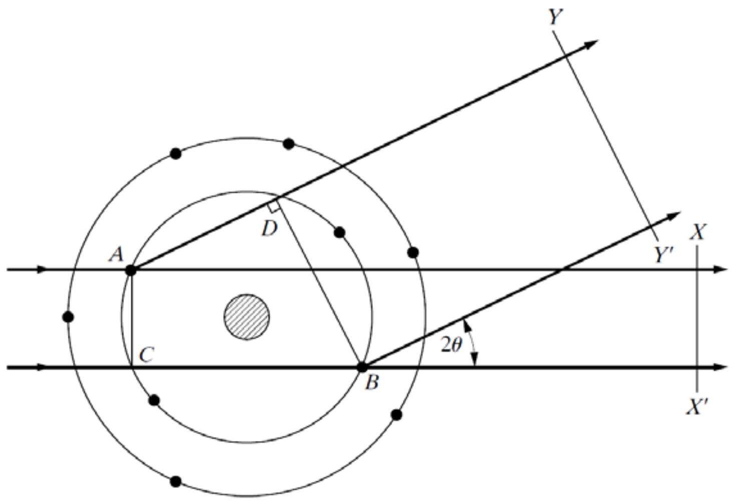
2.1 Theory of the X-ray diffraction in crystalline material

When incoming x-ray incident on the crystal surface, it penetrates and interact with the electron cloud of the atoms which are periodically arranged in the crystal. The elastic scattering of the x-ray produces diffraction pattern which in turn provide the information of the crystal. The intensities of the scattered x-ray can be expressed through structure factor.

2.1.1. Atomic scattering factor

An x-ray beam can be described as an electromagnetic wave characterized by an electric field whose strength varies sinusoidally with time at any one point in the beam. Since an electric field exerts a force on a charged particle such as an electron, the oscillating electric field of an x-ray beam will set any electron it encounters into oscillatory motion about its mean position. Now an electron which has been set into oscillation by an x-ray beam is continuously accelerating and decelerating during its motion and therefore emits an electromagnetic wave. In this sense, an electron is said to *scatter* x-rays, the scattered beam being simply the beam radiated by the electron under the action of the incident beam. The scattered beam has the same wavelength and frequency as the incident beam and is said to be *coherent* with it, since there is a definite relationship between the phase of the scattered beam and that of the incident beam which produced it.

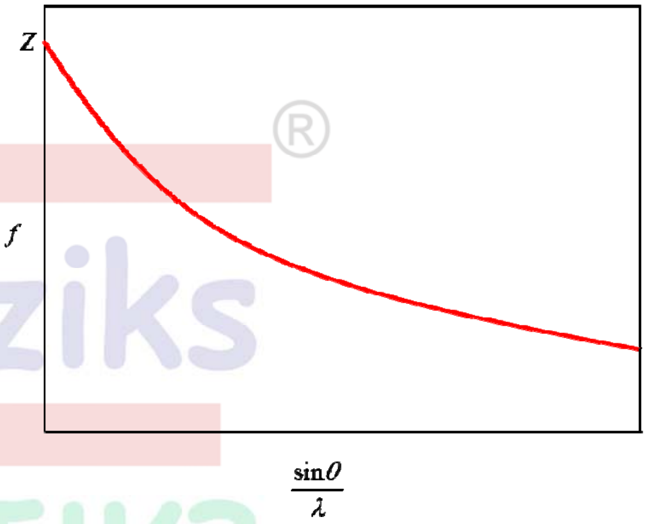
During interaction of x-ray with atom each electron in it scatters part of the radiation coherently. For example, in the figure below, scattered wave from electron A and B along $2\theta = 0$ are in same phase and therefore interference is constructive while along finite 2θ, phase difference is non-zero and partial interference take place with the result that the net amplitude of the wave scattered in this direction is less than that of the wave scattered by the same electrons in the forward direction.



A quantity *f*, *the atomic scattering factor*, is used to describe the "efficiency" of scattering of a given atom in a given direction. It is defined as a ratio of amplitudes:

$$f = \frac{\text{amplitude of the wave scattered by an atom}}{\text{amplitude of the wave scattered by one electron}}$$

The atomic scattering factor depends also on the wavelength of the incident beam: at a fixed value of θ, f will be smaller the shorter the wavelength, since the path differences will be larger relative to the wavelength, leading to greater interference between the scattered beams. It must be noted that, due to zero phase difference between all the scattered waves, the interreference is fully constructive $f = Z$ for any atom scattering in the forward direction. As θ increases, however, the waves scattered by individual electrons become more and more out of phase and f decreases. The actual calculation of f involves $\sin\theta$ rather than θ, so that the net effect is that f decreases as the quantity $\frac{\sin\theta}{\lambda}$ increases.



The scattering factor f is sometimes called the *form factor*, because it depends on the way in which the electrons are distributed around the nucleus.

2.1.2 Geometric Structure Factor:

The intensity of an x-ray beam diffracted from a crystal not only depends upon the atomic scattering factor of the various atom involved but also on the contents of the unit cell. Every atom in the unit cell contributes to every reflection according to its chemical nature and its relative position. Owing to this shift in position relative to the other atoms, the photons contributed by each atom in the unit cell have a phase shift relative to those from other atoms.

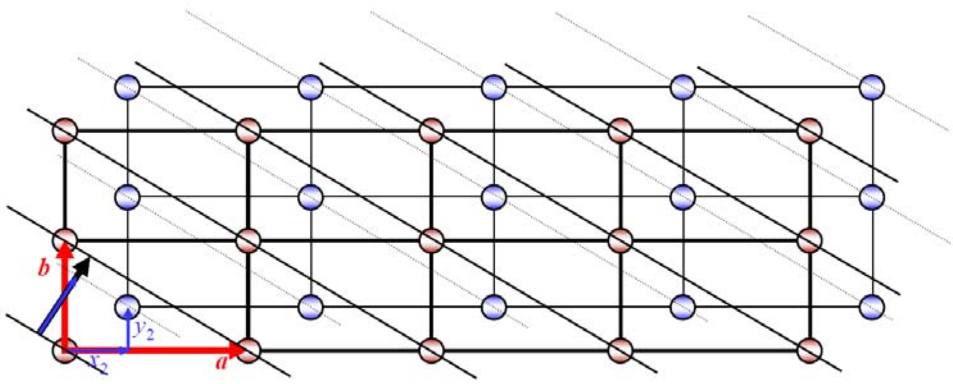
$$\Phi_i = \Delta\Phi_{i(a)} + \Delta\Phi_{i(b)} + \Delta\Phi_{i(c)} = 2\pi\left(hx_i + ky_i + lz_i\right)$$

This makes the structure factor a complex number:

$$F_i = f_i \cdot \exp\left(\Phi_i\right) = f_i\left(\cos\Phi_i + i\sin\Phi_i\right)$$

Every atom i in the unit cell contributes to every structure factor $F(hkl)$ (that is reflection) according to its position in the cell and its chemical nature

$$F(hkl) = \sum_i f_i\left[\cos 2\pi\left(hx_i + ky_i + lz_i\right) + i\sin 2\pi\left(hx_i + ky_i + lz_i\right)\right]$$



This equation may be written more compactly as

$$F(hkl) = \sum_i^N f_i\, e^{2\pi i\left(hx_i + ky_i + lz_i\right)}$$

where the summation extends over all N atoms of the unit cell. F is, in general, a complex number, and it expresses both the amplitude and phase of the resultant wave. Its absolute value $|F|$ gives the amplitude of the resultant wave in terms of the amplitude of the wave scattered by a single electron. Like the atomic scattering factor f, $|F|$ is defined as a ratio of amplitudes:

$$|F| = \frac{\text{amplitude of the wave scattered by all the atoms of a unit cell}}{\text{amplitude of the wave scattered by one electron}}$$

The intensity of the beam diffracted by all atoms of the unit cell in a direction predicted by Bragg's law is proportional simply to $|F|^2$, the square of the amplitude of the resultant beam, and $|F|^2$ is obtained by multiplying the expression given for F in above equation by its complex conjugate F*. Above equation is therefore a very important relation in x-ray crystallography, since it permits a calculation of the intensity of any *hkl* reflection from a knowledge of the atomic positions.

Some Useful Relations:

In calculating structure factors by complex exponential functions, many particular relations occur often enough to be worthwhile stating here

$(a)\ e^{\pi i} = e^{3\pi i} = e^{5\pi i} = -1$

$(b)\ e^{0} = e^{2\pi i} = e^{4\pi i} = +1$

(c) In general $e^{n\pi i} = (-1)^n$, where n is any integer

$(d)\ e^{n\pi i} = e^{-n\pi i}$, where n is any integer

$(e)\ e^{\pi i} + e^{-\pi i} = 2\cos x$

2.1 3 STRUCTURE-FACTOR CALCULATIONS

(1) *Simple cubic crystal:* The simplest case is that of a unit cell containing only one atom at the origin, i.e., having fractional coordinates $(0,0,0)$. Its structure factor is

$$F = fe^{2\pi i(0)} = f$$

And therefore, intensity which is the square of the amplitude is $F^2 = f^2$.

Thus, F^2 is thus independent of h, k & l and the same for all reflection.

All h, k, l is possible in SC.

(2) *Base centered cell*: It has two atoms of the same kind located at 0, 0, 0 & $\frac{1}{2}, \frac{1}{2}, 0$. Its structure factor is

$$F = f[1 + e^{i2\pi(h+k)}]$$

This expression may be evaluated without multiplication by the complex conjugate, since $(h + k)$ is always integral, and the expression for F is thus real and not complex. If h and k are both even or both odd, i.e., "unmixed," then their sum is always even and has the value 1.

Therefore

$F = 2f$, $F^2 = 4f^2$: for h & k unmixed

While $F = 0$, $F^2 = 0$: for h & k mixed

Note : The value of l index has no effect on the structure factor

Present planes are: (111), (112), (113) & (021), (022), (023)

Absent planes are: (011), (012), (013) & (101), (102), (103)

(3) *Body Centered cell*: It has two atoms located at (0 0 0) & $\left(\frac{1}{2}\frac{1}{2}\frac{1}{2}\right)$. Its structure factor is

$$F = f[1 + e^{\pi 2i(h+k+l)}]$$

And $F = 2f$, $F^2 = 4f^2$: when $(h + k + l)$ = Even

While $F = 0$, $F^2 = 0$: when $(h + k + l)$ = odd

Present planes are: (1 1 0), (2 0 0), (2 2 2) etc

Absent planes are: (1 0 0), (1 1 1), (2 1 0) etc

(4) *Face centered cell*: It has four atoms located at (0 0 0), $\left(\frac{1}{2}\frac{1}{2}0\right)$, $\left(\frac{1}{2}0\frac{1}{2}\right)$ and $\left(0\frac{1}{2}\frac{1}{2}\right)$. Its structure factor is

$$F = f\left[1 + e^{\pi 2i(h+k)} + e^{\pi 2i(h+l)} + e^{i2\pi(k+l)}\right]$$

And $F = 4f$, $F^2 = 16f^2$: If h, k, l are unmixed

While $F = 0$, $F^2 = 0$: If h, k, l are mixed

Present planes are: (1 1 1), (2 0 0), (2 2 0) etc

Absent planes are: (1 0 0), (1 1 0), (2 1 1) etc.

Simplified Table:

Bravais lattice	**Reflection possibly Present**	**Reflection necessarily absent**
Simple cubic	All	None
Base centered cubic	h & k unmixed	h & k mixed
Body centered cubic	$(h + k + l)$ even	$(h + k + l)$ odd
Face centered cubic	h, k & l unmixed	h, k & l mixed

Note: (1) The first order reflection from (1 0 0) planes in a bcc crystal is absent, while second order reflections from (1 0 0) plane is present and it is this reflection which appears at the position of the 1st order reflection from (2 0 0) planes.

(2) The ratio of $(h^2 + k^2 + l^2)$ values for all allowed reflection from cubic crystal as obtained from the extinction rules are given as follows.

SC : : 1 : 2 : 3 : 4 : 5 : 6 : 8 : 9 : 10 : 11 : 12

BCC : : 2 : 4 : 6 : 8 : 10 : 12 : 14 : 16 : 18 : 20

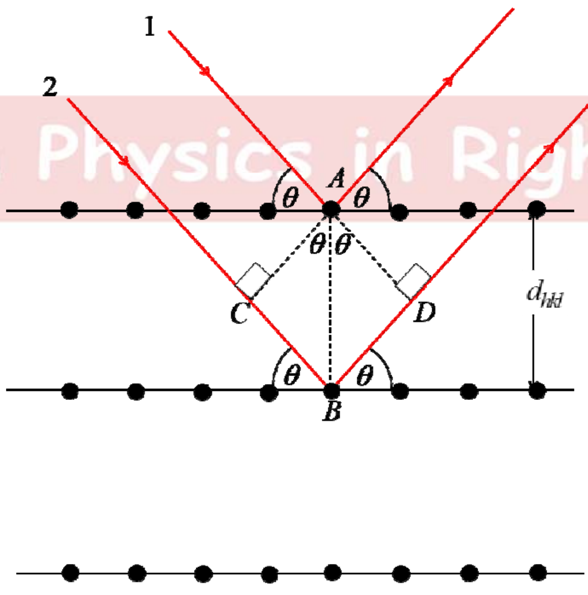
FCC : : 3 : 4 : 8 : 11 : 12 : 16 : 19 : 20 :

DC : : 3 : 8 : 11 : 16 : 19 : 20

3.2 Bragg's Law

X-rays are a form of electromagnetic radiation and these are used for determining the crystal structures are they have high energy and short wavelengths. The wavelengths of x-rays are of the order of the atomic spacing for solids. When a beam of x-rays impinges on a solid material, a portion of this beam will be scattered in all direction by the electrons associated with each atom or ion that lies within the beam path.

Bragg's law is a simple and elegant law which is central to the analysis of diffraction data. This law relates the angle θ (at which there is a maximum in diffracted intensity) to the wavelength λ of X-rays and the inter-layer distance d between the planes of atoms / ions / molecules in the lattice.



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The layers of atoms are indicated by the labels to the right of the lines. The Lattice points are denoted by solid circles. The rays 1 and 2 are parallel and they have the same phase till they are at A and C respectively. The ray 2 traverses an additional distances CBD. This additional distance causes a phase difference between rays 1 and 2. If rays 1 and 2 are at an angle θ of with respect to the atomic planes, then the angles CAB and BAD are also θ and the path length CB and BD are both equal to $d\sin\theta$ where d is the perpendicular distance between any two adjacent layers. For constructive interference between rays 1 and 2, the path difference between 1 and 2 has to be an integral multiple of λ, the wavelength of X-rays used, i.e.,

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

This is known as Bragg's law, n is order of reflection.

The reflection of 1 is called a first order reflection as it is from the first inner layer. The ray 3 which is reflected by layer 3 is a second order reflection. The intensities of reflected light from the inner layers (3, 4 (not shown) and so on) is much less and the major diffraction is brought out by the first inner layer. From the intense peaks of the diffraction patterns, the distances between various crystal planes can be determined.

3.3 Methods of X-Ray Diffraction:

In x-ray diffraction studies, the probability that the atomic planes with right orientations are exposed to x-rays is increased by adopting there of crystal structure studies method.

1) Law Method
2) Rotating Method
3) Powder Method

1) Laue's Technique:

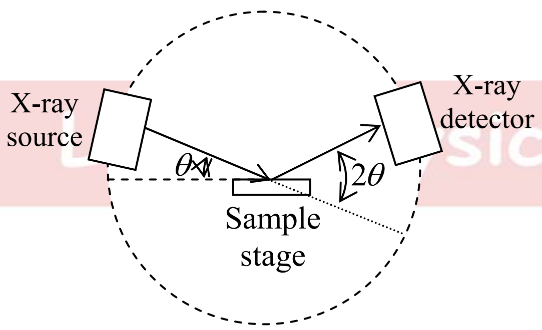
The single crystal is held stationary and a beam of white radiations is inclined on it at a fixed glancing angle θ i.e. θ is fixed while λ is varies different wavelengths present in the white radiations select the appropriate reflecting planes out of the numerous present in the crystal such that the Bragg's condition is satisfied this technique is called the Laue's technique.

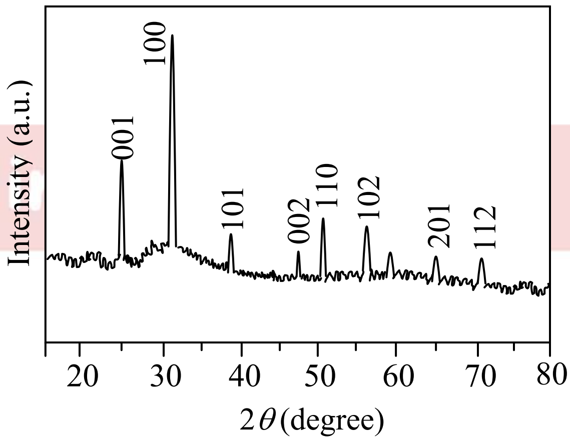
2) Rotating Crystal Method:

A single crystal is held in the path of monochromatic radiations and is rotated about an axis i.e. λ is fixed while θ varies. Different sets of parallel atomic planes are exposed to incident radiations for different values of θ and reflections take place from those atomic planes for which d and θ satisfied the Bragg's law. This method is known as the rotating crystal method.

3) Powder Method:

Modern x-ray crystal analysis uses an x-ray diffractometer which has a radiation counter to detect the angle and intensity of the diffraction beam.





A recorder automatically plots the intensity of the diffracted beam as the counter moves on a Goniometer circle. Figure shows an x-ray diffraction recorder chart for the intensity of the diffracted beam verses the diffraction angle 2θ for a powdered pure metal specimen.

Characteristics of the Bragg's law:

(i). It is the consequence of the periodicity of the space lattice.

(ii). The Bragg's law does not refer to the arrangement or basis of the atoms associated with the lattice points.

(iii). For a given order n and spacing d, the angle θ decreases with decrease in the wavelength λ.

(iv). The relative intensity of the various orders n of diffraction from a given set of parallel planes is determine by the composition of the basis of the crystal results in the change in d. This in turn changes the phase difference between the interfering waves and hence the resulting amplitude. Being proportional to the square of the amplitude the intensity is therefore affected.

(v). Bragg's reflection occur only for the wavelength $\lambda \le 2d$. That's why crystal cannot diffract visible rays.

(vi). For X-ray photons,

$$E = h\nu = \frac{hc}{\lambda} \quad \text{or} \quad \lambda(A^0) = \frac{hc}{E} = \frac{12400}{E(eV)}$$

Therefore, the energy of X-rays of wavelength 1A^0 is 12.4keV.

Electron Diffraction by Crystal:

Louis de Broglie originated the idea that moving electrons may exhibit both particle and wave nature. He proposed that, analogous to photons, the wavelength of the electron is given by

$$\lambda(A^0) = \frac{h}{P} = \frac{h}{\sqrt{2mE}}$$

Where h is the Planck constant, m is the mass of the electron and E is the energy of the electron. Since m = 9.1x10^{-31}kg.

Therefore $\lambda(A^0) = \frac{12}{\sqrt{E}}$

Thus, the energy of electrons of wavelength 1A^0 is 144eV.

Characteristic of Electron Diffraction

(i). Incident electrons are not only diffracted by the electrons but also by the nuclei of the atoms of the crystal. So the electron diffraction is much more intense than X-ray diffraction.

(ii). An electron beam has very low penetration power as it experiences repulsion from atomic electrons. Therefore this technique is useful for thin films.

Neutron diffraction by Crystal:

Using the de-Broglie relation for neutron (mass m=1.675x10^{-27}kg) the associated wavelength

$$\lambda(A^0) = \frac{0.28}{\sqrt{E}}$$

This shows that the energy associated with neutrons of wavelength 1A^0 is approximately 0.08eV. This energy is much less than of X-rays of the same wavelength.

Characteristic of Neutron Diffraction

(i) Neutrons are scattered only by the nuclei of the atoms of the crystal.

(ii) Scattering cross section does not vary with increasing atomic number.

(iii) Lighter elements such as hydrogen and carbon produce strong neutron scattering which is almost absent in X-ray diffraction.

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SOLVED EXAMPLE

Example: At what angle will a diffracted beam emerge from the (111) planes of a face centered cubic crystal of unit cell length $0\cdot 4\,nm$? Assume diffraction occurs in the first order and that the X-ray wavelength is $0\cdot 3\,nm$.

Solution: $n\lambda = \dfrac{2a}{\left(h^2+k^2+l^2\right)^{1/2}}\sin\theta = \dfrac{2\times 0\cdot 4}{\left(1^2+1^2+1^2\right)^{1/2}}\sin\theta$

$$\sin\theta = \frac{0\cdot 3\sqrt{3}}{0\cdot 8} = 0\cdot 6495$$

$$\theta = 40\cdot 5^0$$

Example: Calculate the separations of the sets of plans which produce strong x-ray diffractions beams at angles 4^0 and 8^0 in the first order, given that the x-ray wavelength is $0.1\,nm$.

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

$$d_1 = \frac{1\cdot\lambda}{2\sin\theta} = \frac{0\cdot 1}{2\sin 4^0} = 0\cdot 717\,nm$$

$$d_2 = \frac{0\cdot 1}{2\sin 8^0} = 0\cdot 359\,nm$$

Example: Ar x-ray beam of wavelength $0\cdot 16\,nm$ is incident on a set of planes of a certain crystal. The first Bragg reflection is observed for an incidence angle of 36^0 what is plane What is the plane separation? Will there be any higher order reflections?

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

$$d = \frac{1\cdot\lambda}{2\sin\theta} = \frac{0\cdot 16}{2\sin 30^0} = 0\cdot 136\,nm$$

For $n = 2$

$$\sin\theta = \frac{2\times 0\cdot 16}{2\times 0\cdot 136} = 1\cdot 176$$

a value which is not possible. Thus higher order reflections are not possible.

Example: In the historical experiment of Davisson and Germer electrons of $54\,eV$ at normal incidence on a crystal showed a peak at reflection angle $\theta_r = 40^0$. At what energy neutrons would also show a peak at $\theta_r = 40^0$ for the same order.

Solution: The de Broglie wavelength for electrons is calculated from

$$\lambda = \sqrt{\frac{150}{V}} = \sqrt{\frac{150}{54}} = 1\cdot 66\,A^0$$

Bragg's equation will be satisfied for neutrons of the same wavelength.

$$\lambda = \frac{0\cdot 286}{\sqrt{E}}A^0$$

where E is in eV,

$$E = \left(\frac{0\cdot 286}{\lambda}\right)^2 = \left(\frac{0\cdot 286}{1\cdot 66}\right)^2 = 0\cdot 0297\,eV$$

Example: A copper crystal with FCC structure shows the first diffraction peak at a Bragg angle of 45^0. The wavelength of X- ray used is $1.5\,\overset{0}{\mathrm{A}}$. Calculate the volume of the primitive unit cell of the copper.

Solution: $2d\sin\theta = \lambda$ where $d = \dfrac{a}{\sqrt{h^2+k^2+l^2}}$

In FCC the first diffraction peak appears for (111) plane

$$\therefore d=\frac{a}{\sqrt{1^2+1^2+1^2}}=\frac{a}{\sqrt{3}} \qquad \Rightarrow a=\sqrt{3}d$$

$$\Rightarrow \quad a=\sqrt{3}\times\frac{\lambda}{2\sin\theta}=\sqrt{3}\times\frac{1.5\times10^{-10}}{2\times\sin 45^0}$$

$$\Rightarrow \quad a=\frac{1.73\times1.5\times10^{-10}}{2\times\frac{1}{\sqrt{2}}}=1.84\times10^{-10}m=1.84\overset{0}{\mathrm{A}}$$

The volume of the FCC and cell is

$$V=a^3=\left(1.84\overset{0}{\mathrm{A}}\right)^3$$

The volume of the primitive unit cell of FCC is

$$V'=\frac{V}{N_{eff}}=\frac{(1.84)^3}{4}\left(\overset{0}{\mathrm{A}}\right)^3=\frac{17.6}{4}\left(\overset{0}{\mathrm{A}}\right)^3=1.55\left(\overset{0}{\mathrm{A}}\right)^3$$

Example: Electrons accelerated by $798V$ are reflected from a crystal. The reflection maximum occurs when the glancing angle is 30^0. Calculate the interplanar spacing in the crystal

Solution: X - ray wavelength is

$$\lambda=\sqrt{\frac{150}{V}}A^0=\sqrt{\frac{150}{798}}A^0=\sqrt{0.178}=0.43A^0=4.3\times10^{-11}m$$

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

$$\therefore d=\frac{\lambda}{2\sin\theta}=\frac{4.3\times10^{-11}}{2\times\sin 30^0}=\frac{4.3\times10^{-11}}{2\times\frac{1}{2}}=4.3\times10^{-11}m=0.43A^0$$

Example: Consider a set of crystal planes which are separated by $1.82\overset{0}{\mathrm{A}}$. If X - ray of wavelength $1.54\overset{0}{\mathrm{A}}$ is used, then find number of possible Bragg angles for reflection from these planes

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

For $n=1;\ \sin\theta_1=\frac{\lambda}{2d}$

$$\sin\theta_1=\frac{1.54}{2\times1.82}=0.42$$

For $n=2;\quad \sin\theta_2=2\left(\frac{\lambda}{2d}\right)=0.85$

For $n=3;\quad \sin\theta_3=3\left(\frac{\lambda}{2d}\right)=1.26$

Since $\sin\theta$ can't be greater than 1, hence maximum possible Bragg angles are only 2.

Example: X - ray diffraction spectrum of $Cu(FCC)$ is obtained using $Cu-K_\alpha$ line of wavelength $1.54\overset{0}{\mathrm{A}}$. The first line appears at an angle 84^0. Find the atomic radius of Cu.

Solution: Given $2\theta=84^0\Rightarrow\theta=42^0$

The first peak in FCC appears for plane of indices (111)

$\therefore$ From Bragg's law

$2d\sin\theta = \lambda$ (For $n = 1$)

$$\Rightarrow d = \frac{\lambda}{2\sin\theta} = \frac{1.54\,\overset{0}{A}}{2\times\sin\left(42^0\right)} = \frac{1.54\,\overset{0}{A}}{2\times 0.67} = 1.15\,\overset{0}{A}$$

Since, $d = \frac{a}{\sqrt{h^2+k^2+l^2}} = \frac{a}{\sqrt{1^2+1^2+1^2}} = \frac{a}{\sqrt{3}}$

$$\therefore a = \sqrt{3}d = \sqrt{3}\times 1.15\,\overset{0}{A} = 1.99\,\overset{0}{A}$$

Now, $\sqrt{2}\,a = 4r \Rightarrow r = \frac{\sqrt{2}\,a}{4} = \frac{\sqrt{2}\times 1.99\,\overset{0}{A}}{4} \Rightarrow r = 0.7\times 10^{-10}\,m$

Example: The X - ray diffraction of Diamond cubic gives peak for (311) plane at 64^0. Find the number of XRD peaks below 64^0 angle

Solution: In diamond cubic, the planes giving XRD peaks are (111), (220), (311)

$\therefore$ Below (311) there are only 2 peaks

Example: Calculate the longest wavelength that can be analyzed by a rock salt crystal with interplanar spacing $2.82\,\overset{0}{A}$ in the first order of x - ray diffraction

Solution: $2d\sin\theta = n\lambda \Rightarrow 2d\sin\theta = \lambda$ for $n = 1$

$$\therefore \lambda_{\max} = 2d\sin\left(90^0\right) = 2d = 2\times 2.82 = 5.64\,\overset{0}{A}$$