

**Indian Institute of Technology Madras
Presents**

**NPTEL
NATIONAL PROGRAMME ON TECHNOLOGY ENHANCED LEARNING**

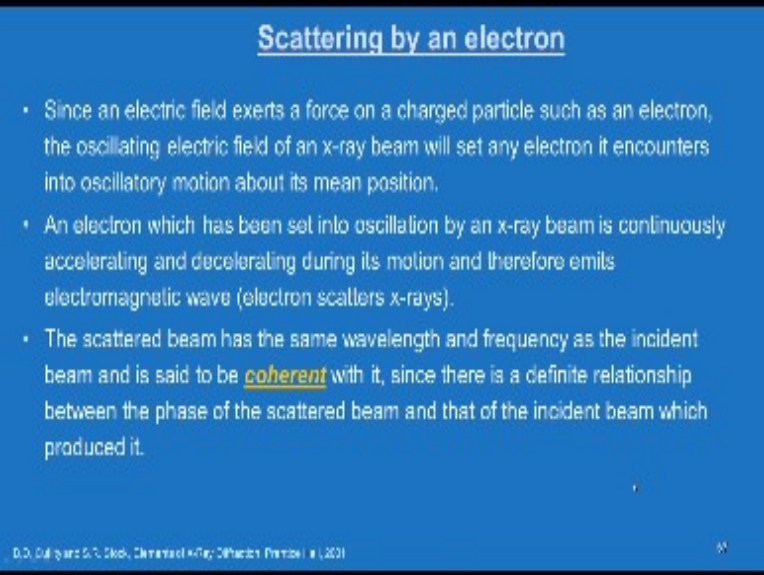
**Lecture-26
Materials Characterization
Fundamentals of X-ray diffraction**

**Dr. S. Sankaran
Associate Professor
Department of Metallurgical and Materials Engineering
IIT Madras
Email: ssankaran@litm.ac.in**

Hello everyone welcome to this material characterization course. In the last class we looked at the X-ray diffraction conditions through Laue equations and we compared that Laue equations with the Bragg's law and then we found that there is a difference in these two laws where the Bragg's law explains the diffraction conditions with the in terms of parallel row of atoms in the planes whereas in the Laue conditions we were able to obtain the diffraction conditions for the rows and net as well as the three-dimensional lattices.

And then we also try to relate the Bragg's law with the reciprocal lattice and we briefly went through the concepts of reciprocal lattice and we also showed or demonstrated how this Ewald's sphere links the Bragg's law with the reciprocal lattice. And then we started discussing about the intensity of X-ray diffraction which is which is what primarily we are interested in probe when we use X-rays as a probing tool to analyze the crystal systems and then in that discussion we were also saying that in order to arrive at the intensity expressions we need to understand how the X-ray scattered by the single electron is understood. So in that direction we will continue our discussion today.

(Refer Slide Time: 02:08)



Scattering by an electron

- 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.
- An electron which has been set into oscillation by an x-ray beam is continuously accelerating and decelerating during its motion and therefore emits electromagnetic wave (electron scatters x-rays).
- 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.

D.D. Guljari & S. S. Ghosh, Diamond X-Ray Diffractometer, 2021 59

So look at this first slide where some of the important remarks about scattering by an electron X-ray scattering by an electron. 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. An electron which has been set into oscillation by X-ray beam is continuously accelerating and decelerating during its motion and therefore emits electromagnetic wave (electron scatters X-rays).

The scattered beam has the same wavelength and the frequency as the incident beam and is said to be coherent with it, since there is a definite relationship between the phase of scattered beam and that of the incident beam which produced it. So we have the definition of what is a coherent beam that means it should have the same wavelength and the frequency as the incident beam, so we also know that what you mean by the phase relations by now.

(Refer Slide Time: 03:37)

Scattering by an electron

- X-rays are scattered in all directions by an electron, the intensity of the scattered beam depends on the angle of scattering.
- J.J. Thomson demonstrated that the intensity I of the beam scattered by a single electron of charge e coulombs (C) and mass m kg, at a distance r meters from the electron, is given by

$$I = I_0 \left(\frac{\mu_0}{4\pi} \right)^2 \left(\frac{e^4}{m^2 r^2} \right) \sin^2 \alpha = I_0 \frac{K}{r^2} \sin^2 \alpha$$

where I_0 = intensity of the incident beam, $\mu_0 = 4\pi \times 10^{-7} \text{ m kg C}^{-2}$, K = constant, and α = angle between the scattering direction and the direction of the acceleration of the electron.

D.D. College of Engineering, Durgam Cheruvu, Hyderabad - 500042

X-rays are scattered in all directions by an electron, the intensity of the scattered beam depends on the angle of scattering. J.J. Thomson demonstrated that the intensity I of the beam scattered by a single electron of charge e coulombs and the mass m in kg at a distance r meters from the electron is given by $I = I_0 (\mu_0 / 4\pi)^2 (e^4 / m^2 r^2) \sin^2 \alpha = I_0 (K / r^2) \sin^2 \alpha$ where I_0 is the intensity of the incident beam μ_0 is equal to $4\pi \times 10^{-7} \text{ m kg / C}^2$, K = constant and α angle between the scattering direction and the direction of the acceleration of the electron.

(Refer Slide Time: 04:41)

Scattering by an electron

Coherent scattering of x-rays
by a single electron

An unpolarized incident beam, such as that issuing from x-ray tube, has its electric vector E in a random direction in the yz plane

$$E^2 = E_y^2 + E_z^2$$

On the average, E_y will be equal to E_z , since the direction of E is perfectly random, therefore

$$E_y^2 = E_z^2 = \frac{1}{2} E^2$$

The intensity of these two components of the incident beam is proportional to the square of their electric vectors, since E measures the amplitude of the wave and the intensity of a wave is proportional to the square of its amplitude

$$I_{Oy} = I_{Oz} = \frac{1}{2} I_0$$

D.D. Gajjar & S. S. Sakh, Elements of Optics, Prentice Hall, 2001

Suppose if you look at this kind of coherent scattering of X-ray by a single electron assuming that this is the coordinate where you have all this electric vectors in the mutual perpendicular direction X, Y, Z and then we can try to account for the intensity of the X-rays scattered by an electron. So look at this remarks an polarized incident beam such as that issuing from X-ray tube has its electric vector E in a random direction in the YZ plane $E^2 = E_y^2 + E_z^2$. On the average E_y will be equal to E_z since the direction of E is perfectly random therefore we can assume $E_y^2 = E_z^2 = (1/2) E^2$.

The intensity of these two components of the incident beam is proportional to the square of their electric vectors. Since E measures the amplitude of the wave and the intensity of your wave is proportional to square of its amplitude, so we can write the intensity expression like this $I_{Oy} = I_{Oz} = (1/2) I_0$ with respect to this schematic.

(Refer Slide Time: 06:18)

Scattering by an electron

The y component of the incident beam accelerates the electron in the direction O_y . It therefore gives rise to a scattered beam whose intensity at P is found from the above equation to be

$$I_{Oy} = I_{Oy} \frac{K}{r^2}$$

since $\alpha = \angle yOP = \pi/2$. Similarly, the intensity of the scattered z component is given by

$$I_{Oz} = I_{Oz} \frac{K}{r^2} \cos^2 2\theta$$

D.D. Gajjar & S.V. Shrivastava, Department of Physics, Pimpri Chinchwad Education Trust, Pimpri, Maharashtra, India

The y component of the incident beam accelerates the electron in the direction O_y . It therefore gives rise to a scattered beam whose intensity at P is found from the equation to be **$I_{Py} = I_{Oy}(K/r^2)$** . Since $\alpha = \angle yOP$ which is equal to $\pi/2$. Similarly the intensity of the scattered z component is given by **$I_{Pz} = I_{Oz}(K/r^2) \cos^2 2\theta$** .

(Refer Slide Time: 06:57)

Scattering by an electron

Since $\alpha = \pi/2 - 2\theta$. The total scattered intensity at P is obtained by summing the intensities of these two scattered components:

$$\begin{aligned} I_p &= I_{2\theta} + I_p \\ &= \frac{K}{r^2} (I_{0y} + I_{0z} \cos^2 2\theta) \\ &= \frac{K}{r^2} \left(\frac{I_0}{2} + \frac{I_0}{2} \cos^2 2\theta \right) \\ &= I_0 \frac{K}{r^2} \left(\frac{1 + \cos^2 2\theta}{2} \right) \end{aligned}$$

This is the **Thomson equation** for the scattering of an x-ray beam by a single electron.

D.O. Collins and S. S. Skol, *Journal of Optics: Photonics* 1 (2011) 61

And we can look at the other expressions since $\alpha = \pi/2 - 2\theta$ the total scattered intensity at P is obtained by summing the intensity of these two scattered components $I_p = I_{py} + I_{pz}$ which we can substitute in this form $K/r^2 (I_{0y} + I_{0z} \cos^2 2\theta)$ and then we can rearrange them into $I_0(K/r^2) ((1 + \cos^2 2\theta)/2)$. This is the Thomson equation for the scattering of an X-ray beam by a single electron.

(Refer Slide Time: 07:51)

Scattering by an electron

$$\frac{1}{2}(1 - \cos^2 2\theta) \longrightarrow \text{Polarization factor}$$

If monochromator is used with the diffractometer, then

$$\frac{1}{2}(1 + \cos^2 2\theta \cos^2 2\theta_M)$$

D.S. Chakrabarti, S.C. Saha, Chandra Sekhar Ghoshal, Physics, Kolkata, 1991

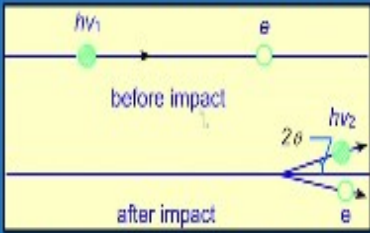
Where $\frac{1}{2}(1 + \cos^2 2\theta)$ is called a polarization factor which we will be incorporating in all the intensity equation whenever we are going to write. If monochromator is used with the diffractometer then this expression is modified into this form that is $\frac{1}{2}(1 + \cos^2 2\theta \cdot \cos^2 2\theta_M)$.

(Refer Slide Time: 08:24)

Scattering by an electron

Compton effect – Elastic collision of photon and electron

It occurs whenever stream of x-ray quanta or photons encounter loosely bound or free electrons.



The diagram illustrates the Compton effect. It is divided into two horizontal sections: 'before impact' and 'after impact'. In the 'before impact' section, a photon with energy $h\nu_1$ (represented by a green dot) moves from left to right, and an electron (represented by a yellow dot) is at rest. In the 'after impact' section, the photon has scattered at an angle 2θ and has a lower energy $h\nu_2$. The electron has recoiled, moving away from the collision point.

The wave length λ_2 of the scattered radiation is thus slightly greater than the wavelength λ_1 of the incident beam, the magnitude of the change being given by the equation

$$\Delta\lambda (\text{\AA}) = \lambda_2 - \lambda_1 = 0.0486 \sin^2 \theta$$

D.O. Gajjar and S. S. Joshi, Department of Physics, Chhatrapati Pratibha Institute, 1, 2021

Now we will look at another form of scattering which is called a Compton Effect which describes the elastic collision of photon and electron. It occurs when the stream of X-ray quanta or photons encounter loosely bound or free electrons, so there is a slightly different from what scattering which we talked about previously and here it is the X-ray quanta we are talking about quanta which encounters a loosely bound or free electrons. Like two billiard balls which are colliding with each other something like that. So you have the $h\nu_1$ is colliding with an electron before impact like this then after impact it goes like this into two different directions.

The wavelength λ_2 of the scattered radiation is thus slightly greater than the wavelength λ_1 of the incident beam the magnitude of the change being given by the equation $\Delta\lambda (\text{\AA}) = \lambda_2 - \lambda_1 = 0.0486 \sin^2 \theta$.

(Refer Slide Time: 09:43)

Scattering by an atom

- When an x-ray beam encounters an atom, each electron in it scatters part of the radiation coherently in accordance with the Thomson equation.
- However, the nucleus has extremely large mass relative to that of the electron and cannot be made to oscillate to any appreciable extent: In fact, the Thomson equation shows that intensity of coherent scattering is inversely proportional to the square of the mass of the scattering particle.
- The net effect is that coherent scattering by an atom is due to only the electrons contained in that atom.

D.O. Collins and S. S. Skol, Chemical X-Ray Diffraction, Prentice Hall, 2001

64

So when an X-ray beam encounters an atom each electron in it scatters part of the radiation coherently in accordance with the Thomson equation. However the nucleus has extremely large mass relative to that of the electron and cannot be made to oscillate to any appropriate extent. In fact: the Thomson equation shows that intensity of coherent scattering is inversely proportional to the square of the mass of the scattering particle.

The net effect is that coherent scattering by an atom is due to only the electrons contained in that atom.

(Refer Slide Time: 10:28)

Scattering by an atom

- Is the wave scattered by an atom simply the sum of the waves scattered by its component electrons?
- More precisely, does an atom of atomic number Z , i.e., an atom containing Z electrons, scatter a wave whose amplitude is Z times the amplitude of the wave scattered by the single electron?
- The answer is **YES**!

If the scattering is in the forward direction, because the waves scattered by all the electrons of the atom are then in phase and the amplitudes of all the scattered waves can be added directly.

D.S. Gill and S.T. Sirohi, Elements of Optics, Prentice Hall, 2001

69

So now we have to ask some questions. Is the wave scattered by an atom simply the sum of the wave scattered by its component electrons? More precisely does an atom of an atomic number Z that is an atom containing Z electrons scatter a wave whose amplitude is Z times the amplitude of the wave scattered by the single electron? The answer is, yes. If the scattering is in the forward direction because the wave scattered by all the electrons of this atom are in phase and the amplitudes of all the scattered waves can be added directly.

See you have to understand this point very important. When we talk about a phase relation also we mentioned this aspect, if the scattering is in the forward direction for example we will look at one schematic about it and since all the waves will be in the same phase they will contribute to the intensity. But in reality it is not so. You will have and we will have at least in this case the electrons will be there in different-different directions an atom.

But the atoms which are supporting the or forward scattering phenomenon they will contribute more to the intensity. So that is the point we are going to prove in the coming schematic.

(Refer Slide Time: 12:12)

Scattering by an atom

- The waves scattered in the forward direction by electrons A and B are exactly in phase on a wave front such as XX' , because each wave has traveled the same distance before and after scattering.
- The other scattered waves shown, have a path difference equal to $(CB-AD)$ and are thus somewhat out of phase along a wave front such as YY' , the path difference being less than one wavelength.

D.O. Colliparc S. S. Skol, Cleveland State University, Physics Department © 2001

So look at this schematic this is a nucleus and you have the electrons in the orbits and then you look at this a green line where the forward scattering rays are shown and they are meeting this wave front XX' and then you have the X-ray scattered in the other direction which are meeting in the YY' wave front and now you know how to relate this a path difference we have looked at those details and much more examples we have seen, so now let us with respect to this schematic let us look at the remarks.

The waves scattered in the forward direction by electrons A and B are exactly in phase on your wave front such as XX' here because each wave has traveled the same distance before and after scattering. The other scattered waves shown have a path difference equal to $CB-AD$ that is $CB-AD$ is the path difference and are thus somewhat out of phase along a wave front such as YY' . The path difference being less than one wavelength, so they are going to scatter slightly different.

(Refer Slide Time: 13:49)

Scattering by an atom

- Partial interference occurs between the waves scattered by A and B, 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

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

- $f = Z$ for any atom scattering in the forward direction. As θ increases, the waves scattered by individual electrons become more and more out of phase and f decreases.

D.D. Phillips & S. T. Shik, Elements of X-Ray Diffraction, Prentice Hall, 2001

Only partial interference occurs between the waves scattered by A and B with the result that the net amplitude of the waves scattered in this direction is less than that of the wave scattered by the same electrons in the forward direction. So this is the fundamental point we have to capture. So the waves which are not in the forward direction they are not going to contribute equally to the interference so only a partial interference will occur between this waves and then they will contribute to some extent to the net amplitude of the wave scattered in that all directions.

Here we have shown only one direction of that nature. We have to imagine that these kind of a partial interference will occur in most of the most of the other directions as well and then finally you get a net amplitude that is a point you have to understand which is going to contribute to the integrated intensity. We will we will just talk about this integrated intensity because that is what we are interested.

So right now you just appreciate this point how the forward scattering waves how they contribute or how about other rays which are contributing partially to the intensity.

(Refer Slide Time: 15:27)

Scattering by an atom

- Partial interference occurs between the waves scattered by A and B, 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

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

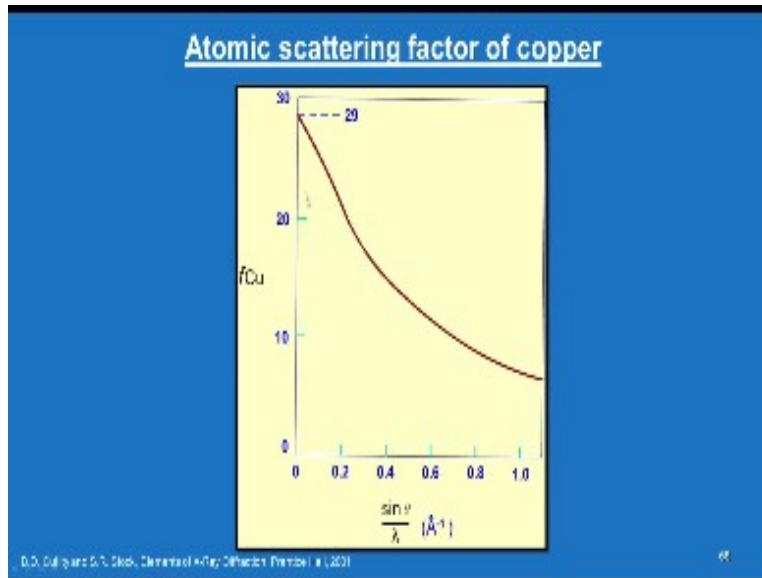
- $f = Z$ for any atom scattering in the forward direction. As θ increases, the waves scattered by individual electrons become more and more out of phase and f decreases.

D.D. Alliyev & T. Slob, Department of Physics, University of Cambridge, 2021

So a quantity 'f' the atomic scattering factor is used to describe the efficiency of the scattering of a given atom in a given direction, where **f = (amplitude of the wave scattered by any atom)/ (amplitude of the wave scattered by one electron)**. Suppose if f is equal to Z for any atom scattering in the forward direction as θ increases the wave scattered by the individual electrons become more and more out of phase and f decreases.

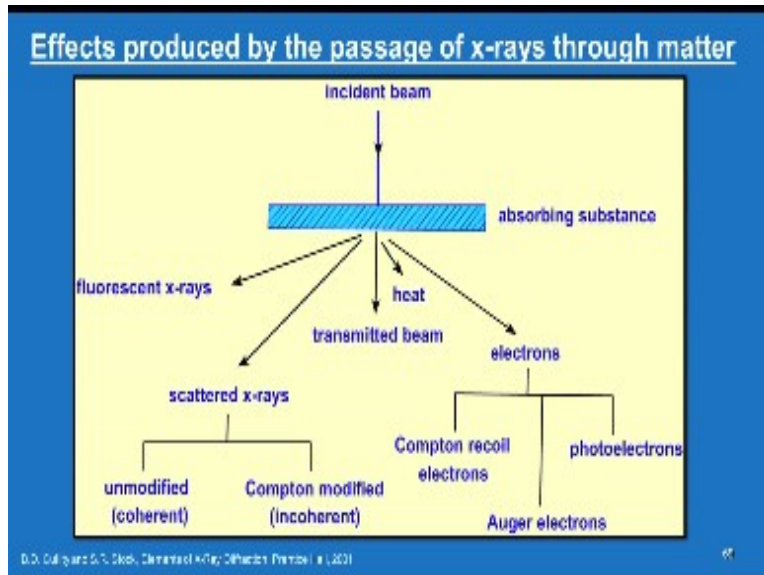
So it is not just that you have all the electrons will be doing only forward scattering and then you will get a maximum intensity but it also depends upon the θ , so that is the point we are now explaining here.

(Refer Slide Time: 16:20)



This is for the atomic scattering factor of copper where you see that as the θ increases in fact it is not θ it is $\sin\theta/\lambda$ which decreases as the θ increases you can see that atomic scattering factor also decreases so this is very important point.

(Refer Slide Time: 16:47)



And now we will just look at the whole picture. Effects produced by the passage of X-rays through a matter in general. You have the incident beam and this is your specimen absorbing some of the X-rays will be absorbed and some will release as a heat and then you have fluorescent X-rays coming out and then you have scattered X-rays and you have electrons coming out you have Compton recoil electrons and photoelectrons and Auger electrons of these three category all the possibilities when you talk about the scattered X-rays you have unmodified coherent scattering the other one is a Compton modified incoherent scattering. These are the two things we have seen today one is coherent scattering other was incoherent scattering.

In one case we see that after the collision the wavelength is changed you get that means they up because of the collision the energy is lost in the form of kinetic energy. So the λ is slightly increased that is what we have seen in that expression where it is called a Compton Effect. It is an incoherent scattering, the previous one where Thomson equation explains the coherent scattering. So these are the two kinds of scattering just for your clarification.

(Refer Slide Time: 18:24)

Structure Factors

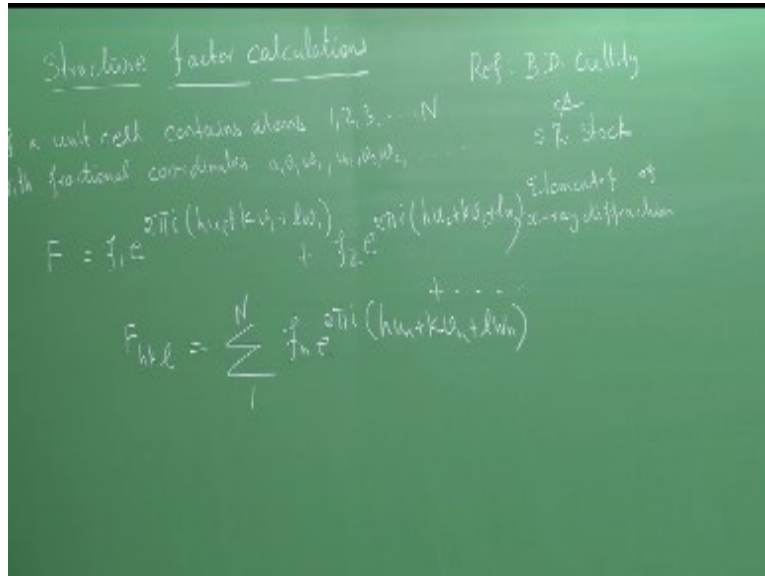
Development

$$F_{hkl} = \sum_{\text{unit cell}} \frac{1}{N} f_n e^{(2\pi i/\lambda)(s-s_0) \cdot r_n}$$
$$\frac{(s-s_0)}{\lambda} = r_{hkl}^* = hb_1 + kb_2 + lb_3$$
$$r_n = u_n a_1 + v_n a_2 + w_n a_3$$
$$F_{hkl} = \sum_n f_n e^{2\pi i(hu_n + kv_n + lw_n)}$$

ANTON D. KRAVITZ Introduction to Diffraction in Materials Science and Engineering, 3rd Edition, Wiley

Now we will look at the structure factors which is very important for the intensity calculations. So the expressions which I have written all here all look familiar to you. The first one is the we have seen from the structure factor expression F_{hkl} is the atomic scattering factor from all the atoms in the unit cell. We will quickly look at this in few minutes what is the details here and this expression is the diffraction vector expression which we have seen yesterday and this is a reciprocal lattice vector and here this is a real lattice vector here which is given and then this form is the final form you get for the structure factor calculations and we will now take up some few examples how to use this and how this the equation gives the intensity for a given crystal system then how they contribute to the total diffraction intensity.

(Refer Slide Time: 19:50)

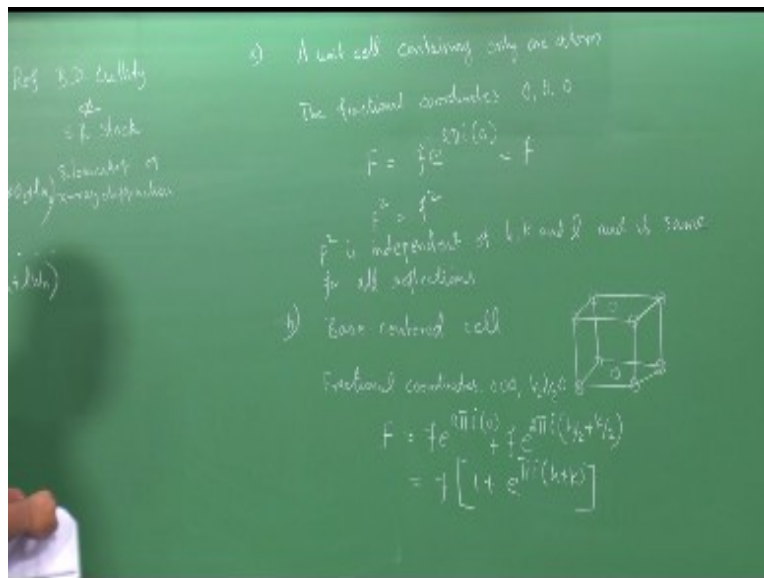


So I will go to the blackboard and then. So what I have written is if a unit cell contains atoms 1, 2, 3 up to the N atoms with the fractional coordinates $(u_1, v_1, w_1), (u_2, v_2, w_2)$ etc then the atomic all the atomic scattering factors from that unit cell should be added like this and then if you sum it up and then that final equation appears like this. So this is the summation of all the atomic scattering factors multiplied by $e^{2\pi i(hu + kv + lw)}$ again so on. I believe that you now appreciate this expression this is atomic scattering factor and then this is this complex exponential function we referred a scattered electromagnetic radiation.

In this case it is X-ray is expressed in terms of complex exponential function and this is coming from the phase difference, but also we have seen before this particular component is coming from a phase difference and this is the structure factor from the unit cell expression. So now we will apply this expression for individual unit cell, we will take it up a simple case and I have taken this from this book B D Cullity and S R Stock and you can go through for the entire description and much more detailed information is given there. And you can also note down certain important relationship mathematical relationship in order to understand some of the factors which will come in between. So first let us go through that.

You can write some of the useful expressions like this you can keep in mind before we look at all the derivation for structure factor for a given crystal system. The $e^{\pi i}$ which is equal to $e^{3\pi i}$ is equal to -1 and if it is $e^{2\pi i}$ an even number $e^{4\pi i}$ or $e^{6\pi i}$ is equal to 1 in general this is the expression $e^{n\pi i}$ is equal to -1 to the power n where n is an integer. Similarly we have $e^{-n\pi i}$ is equal to $e^{-n\pi i}$ where n is any integer and you have this expression as well $e^{i\pi} + e^{-i\pi} = 2\cos x$.

(Refer Slide Time: 28:45)

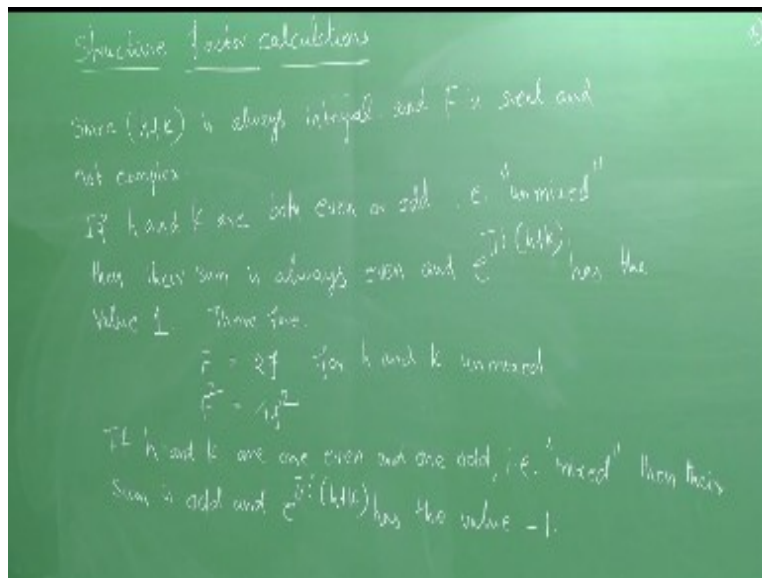


So now we will take up an individual expression I mean unit system. Unit cell system containing only one atom. So if you take up this expression the fractional coordinates (0,0,0) and the structure factor is $F = f \cdot e^{2\pi i(0)}$ which is equal to f and $F^2 = f^2$. F^2 independent of so if you consider a unit cell containing only one atom then the fractional coordinates can be the origin one I mean (0,0,0) and then if you substitute that into this structure factor equation then you see that $F = f \cdot e^{2\pi i \cdot 0}$ which is f because this component becomes 1 and then you get capital F = f. This is a intensity which is independent of hkl and is same for all reflections.

So now we will take up the one more example which is having 2 atoms per unit cell. You is something like this a base centered unit cell and how do we calculate the structure factor. The usual we will start with the fractional coordinates means atoms located in the coordinates for this

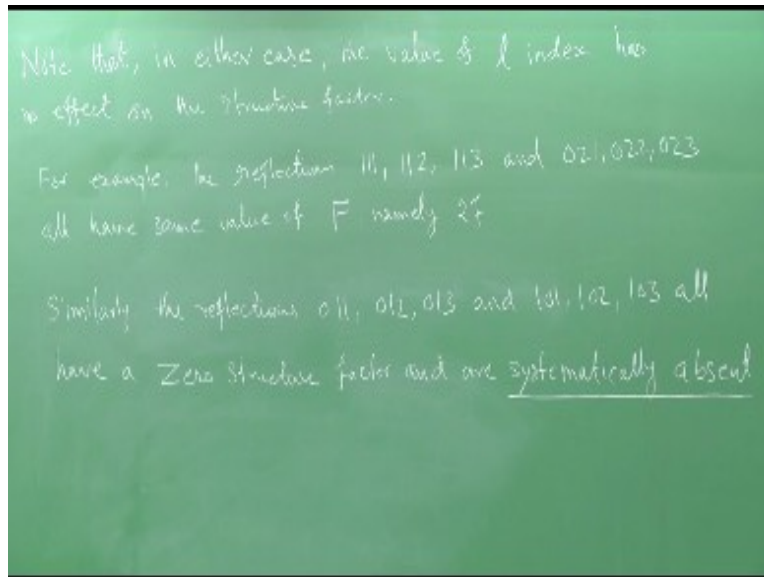
particular position is you have (0,0,0) and (1/2,1/2,0) these are the fractional coordinates you can see that (0,0,0) position this is (1/2,1/2,0) position and then you can write the expression as usual F is equal to. So you get the expression like this, substitute this fractional coordinate into the structure factor equation and then you simplify this you get $f(1+ e^{\pi i(h+k)})$. So we will write something about this expression.

(Refer Slide Time: 34:50)



So this expression may not be multiplied by the complex conjugate because $h+k$ is always the integral and F is a real and not complex. So this is the first step we have to understand and then what is the implication of this condition. The implication is if h and k are both even or odd that is unmixed indices, then their sum will always be an even and the implication of this condition is if h and k are both even or odd that is unmixed indices, then their sum will always be an even your $e^{\pi i(h+k)}$ has the value of 1. Therefore you have $F=2f$ for h and k and mixed and $F^2=4f^2$ if h and k are one even and one odd that is mixed indices then their sum is all sum is odd and $e^{\pi i(h+k)}$ has the value of -1.

(Refer Slide Time: 40:03)



So this is the condition and we can now see that some of the indices what kind of reflection it will give. So if you apply this rule we can note that in either case the value of l index has no effect on the structure factor, so that is what we are seeing here in both cases the indices l do not have any effect. For example if we can take the reflections $(111), (112), (113)$ and $(021), (022), (023)$ all have same value of F namely $2f$. And similarly if you take reflections $(011), (012), (013)$ and $(101), (102), (103)$ all have 0 structure factor and are systematically absent. So this is how you realize how the atom position contributes to the intensity through the structure factor.

So this is one example similarly you can apply the similar conditions for a simple cubic system where you have body centered cubic lattice as well as face centered cubic lattice you can apply this and then realize that how the structure factor varies. We can look at couple of examples and also some of the ordered crystals. We will apply this rule and then calculate the structure factor in the next class, thank you.

IIT Madras Production

Funded by

Department of Higher Education

Ministry of Human Resource Development

Government of India

www.nptel.ac.in

Copyrights Reserved