X-Ray Crystallography

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Lecture -15
Intensity of Diffracted Beams

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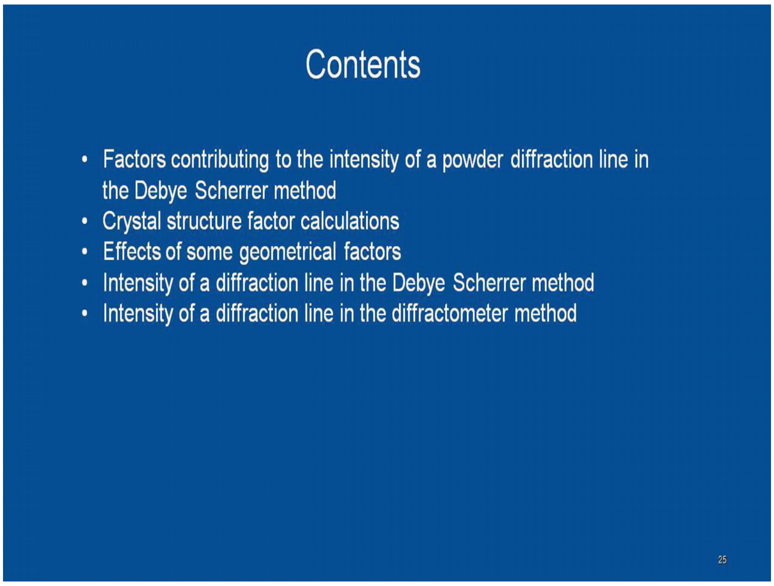

In this lecture, I shall deal with the various factors which affect the intensities of the diffracted beams from a specimen. Say for example, if we look at the X-ray diffraction pattern from a powder camera we find that there are large numbers of diffraction lines.

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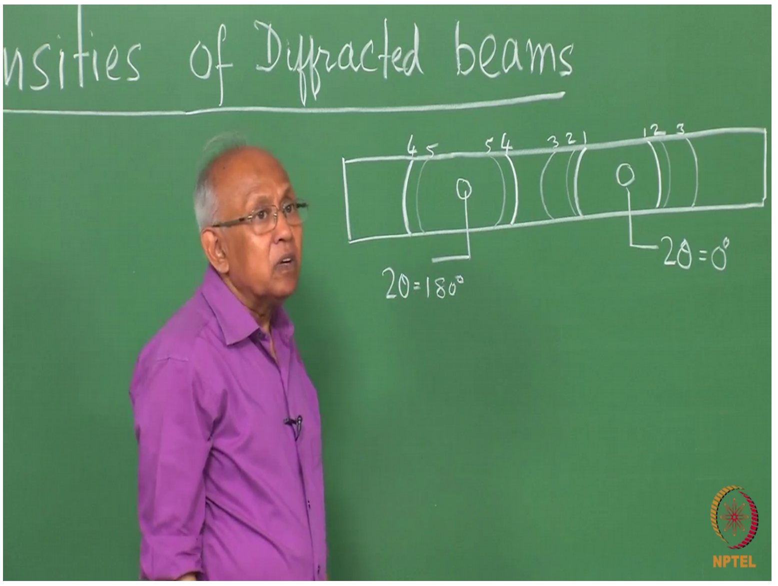

Now each line pair is due to diffraction from a particular h k l plane. Now what we observe is that these line pairs they are not of the same intensity some are many strong, some are reasonably strong, some are weak, some are very weak. Now what is the reason for the difference in the intensities of the diffraction lines? So, in this lecture I am going to discuss those factors which affect the intensities of diffraction lines in a diffraction pattern.

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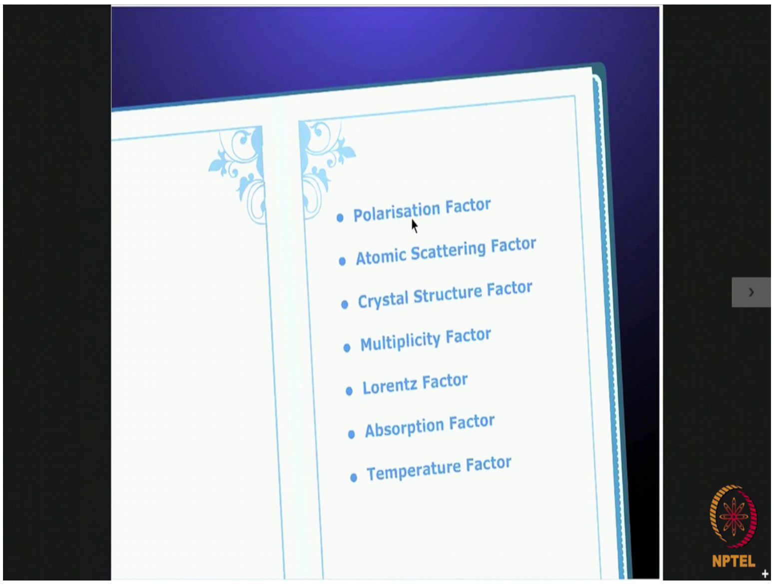

Now, there as various factors which play a role in determining the intensity of a diffraction line: and those have been written down here namely: polarization factor, atomic scattering factor, crystal structure factor, multiplicity factor, Lorentz factor, absorption factor, and temperature factor. Now I will discuss each of these factors separately.

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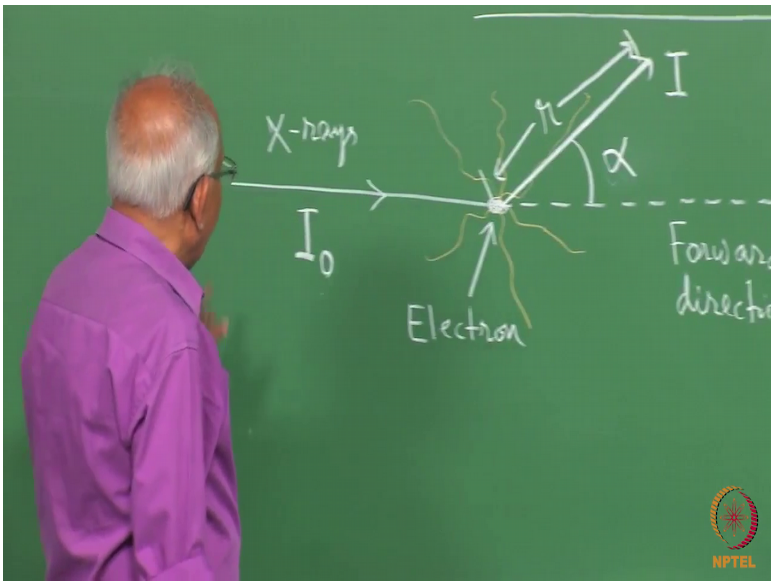

Now, we know that when we have an atom or say the when we consider an electron in an atom and if we allow a beam of X-rays to fall on this electron if we allow a beam of X-rays to fall on this electron then what will happen this electron will act as a scattering centre and it will start scattering the radiation in all possible directions. So, this is what is known as the forward direction of scattering. Say for example, if we want to find out the intensity of the scattered radiation in a particular direction say given by this which makes an angle of theta with the forward direction or I should let me write it as alpha. So, that it does not confuse with the Bragg angle.

Say we want to find out what is the intensity scattered in a particular direction making an angle alpha with the forward direction.

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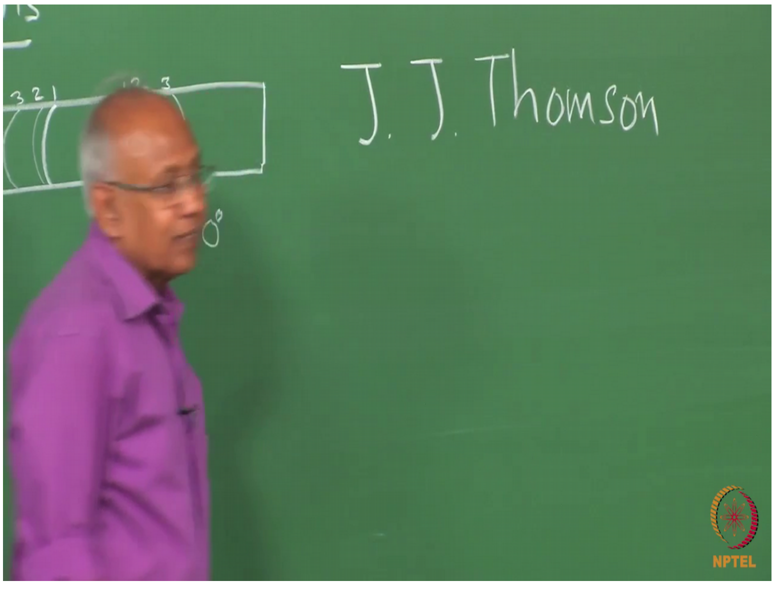

Now, this has already been given by Sir. J. J. Thomson. So, he has given this relationship I equal to I 0 e to the power 4 by r square m square c 4 into sin square alpha.

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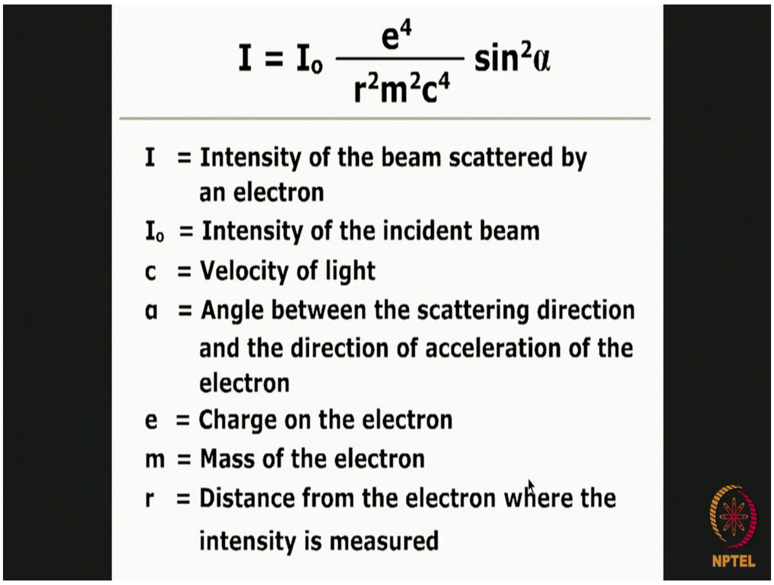

So, here I stands for intensity of the beam scattered by the electron in a direction alpha I 0 is the incident intensity c is the velocity of light alpha is a angle between the scattering direction and the direction of acceleration of the electron or the forward direction e is a charge on the electron m is the mass of the electron and r is the distance from the electron where the intensity is measured; that means, r is this distance.

So, according to J. J. Thomson if an X-ray beam of intensity I 0 is incident on an electron then the intensity that will be scattered in a direction alpha with the forward direction at a distance r from the electron will be given by this explanation.

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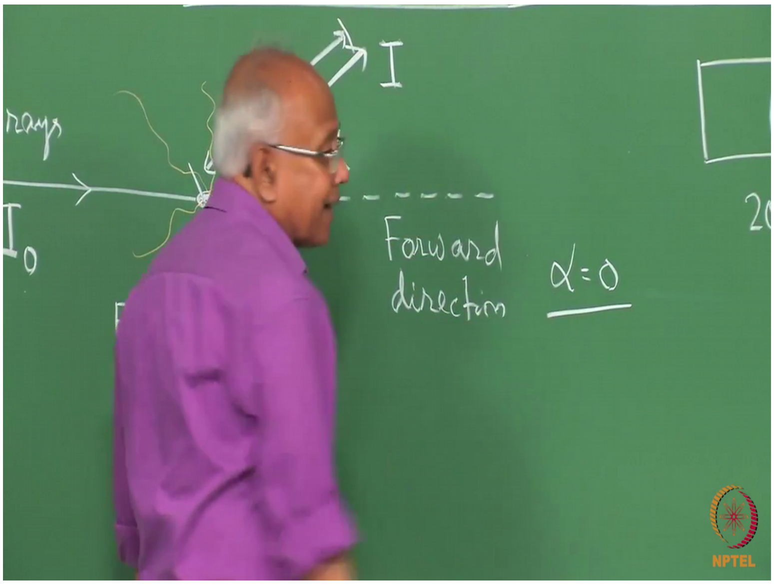

So, you say that the amount of X radiation the intensity of X radiation scattered in different directions will be very different and when it is in the forward direction. That means, for the forward direction alpha is equal to 0 in the forward direction alpha is equal to 0. Now the first factor which I am going to discuss is the polarization factor. Now this factor arises simply because of the fact that the electric vector associated with an X-ray beam is not plane polarized.

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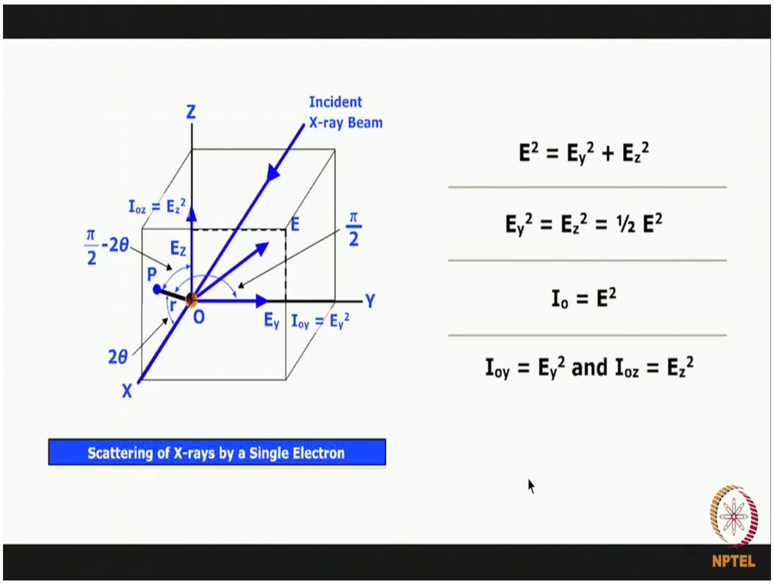

Say for example, we have an electron over here at the origin of this cube suppose a beam of X-rays is incident in this particular direction along the x direction. Now the electrical vector associated with this beam of X-rays can be is e which can be resolved into 2 components E y along the y component and E z along the z component now the intensity of the electrical electric field component along y will be square of E y to the E y square the intensity of the z component of the electric field is equal to E z square.

Now, since the electric field is un-polarized; that means, it can be in any direction in the y z plane statistically there is no reason why E y and E z will be different. So, we will take then to equal. Now, we can write E square is equal to E y square plus E z square now as I said statistically E y and E z should be the same, because the electric field E is un-polarized it can take any position along the in the y z plane. So, we can write E y square is equal to E z square which is equal to half of E square. So, we know that intensity is square of the amplitude.

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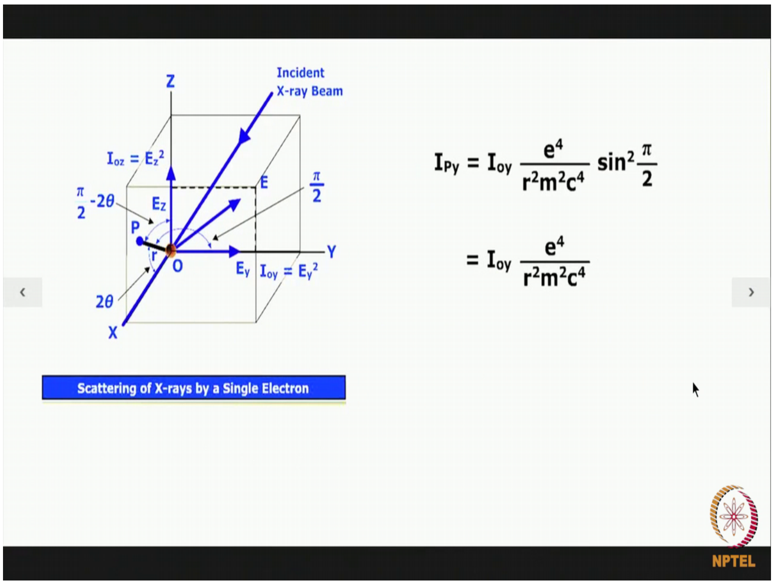

So, electric field amplitude if it is E; we can write I 0 is equal to e square. So, we can write I 0 y intensity of the field along the y direction E y square and I 0 z the intensity of the electric field in the z direction is E z square. Now if we denote a point p in the x z plane and if we want to find out the intensity of the radiation scattered by these electron at the point p, then we can find it out in this way first we find out how much is this scattered radiation from the Y component of the field and how much is the scattered radiation due to the Z component of the field and then add them up.

Now, this angle here because this plane is perpendicular to this plane. So, this angle here is pi by 2 and this angle here is pi by 2 minus 2 theta, because after all what is the angle 2 theta is the angle between the incident direction and the scattered direction. So, this angle is pi by 2 minus 2 theta, and this angle is pi by 2. So, the intensity at the point p due to the y component of the electric field I p y. According to Thomson's equation we can write down as equal to I o I the intensity of the electric field in the y direction e to the power 4 divided by r square m square c 4 in to sin square pi by 2. So, this is equal to I 0 y e to the power 4 by r square m square c 4.

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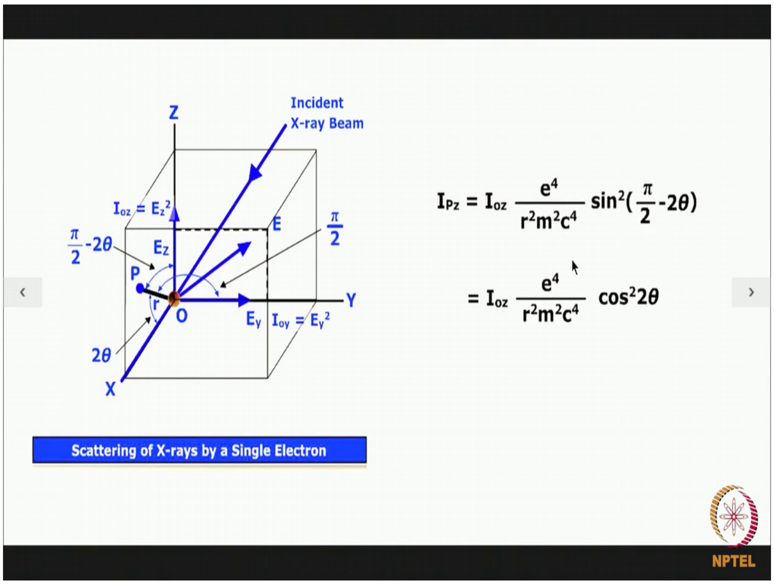

Now what will be the intensity of the scattered radiation by the electron at the point p due to the Z component of the electric vector it will be I o z into e to the power 4 by r square m square c 4 sin square pi by 2 minus 2 theta. So, it will be I o z e to the power 4 by r square m square c 4 the whole thing into sin square 2 theta.

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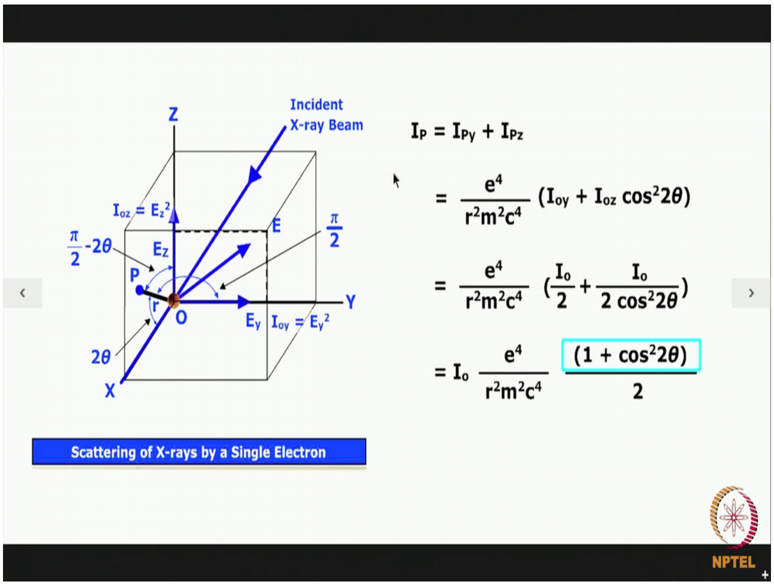

So, the total intensity scattered by the electron at the point p in the x z plane will be equal to I p y plus I p z. So, if we add those 2 up we come to this situation, it will be equal to I 0 e to the power 4 by r square m square c 4 the whole thing multiplied by 1 plus cosine square 2 theta divided by 2.

So, in this equation we find you know so for as the particular point is concerned the only thing which is a variable is cosine square 2 theta. So, depending on the angle which the scattered radiation makes with incident radiation the value of the intensity will change now this is a constant and you know these are all constant.

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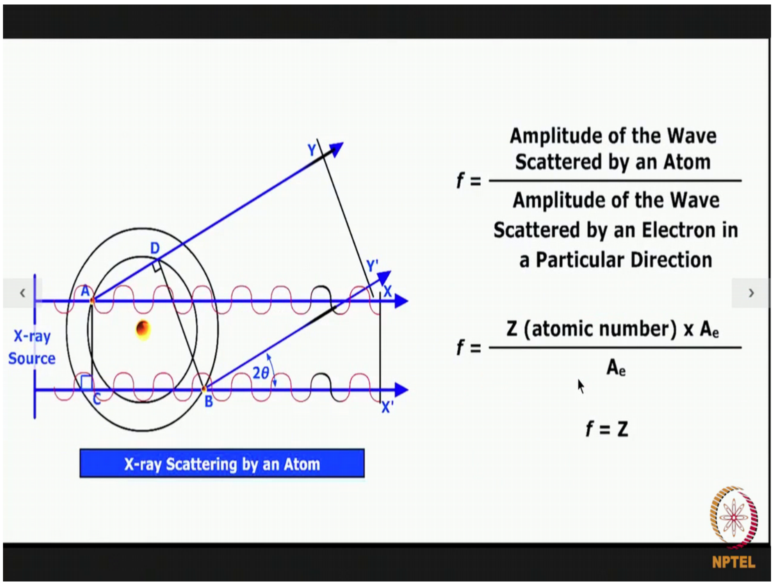

And if we are talking about you know a point at a particular distance r the only thing that is variable is this part of the equation now let us talk about the process of scattering of X-rays by an atom an atom contains a large number of electrons, specially if you have a heavy metal like uranium there are we know that there are 92 electrons if we talk about hydrogen it is only 1 atom per atom. So, the amount of x radiation scattered by an atom will depend on how many scattering centres are there in that atom you see the scattering of x radiation by an atom of a metal is such that the nucleus of the atom does not take part in the process.

The nucleus of an atom is too heavy compared to be mass of an X-ray photon and that is the reason why X-rays do not interact with the nucleus. So, X-rays will interact only with the extra nuclear electrons. So, one thing is very clear that if we have a an element with a higher atomic number that is supposed to scatter X radiation more than an element whose atomic number is lower. Now let us see how to find out the amount of X radiation scattered by an atom with a number of electrons in it.So, we define a quantity we call it the atomic scattering factor f small f is equal to amplitude of the wave scattered by an atom divided by amplitude of the wave scattered by electron; electron you know you I should be written in the same direction you know I would write in the same direction.

So, small f or atomic scattering factor is amplitude of X-ray wave scattered by an atom scattered by all the electrons in the atom divided by amplitude of the wave scattered by a single electron in the same direction. So, it is equal to in case of only when this scattering is taking place in the forward direction. So, this is the forward direction as you can see you know this is an atom these are the atomic shells. So, a beam of X-rays falls on it and interacts with all the electrons. So, if we consider only the scattering talking place in the forward direction then this is equal to z the atomic number multiplied by A e is the amplitude of X-ray radiation scattered by single electron divided by A e. So, f is equal to z.

So, this is true only when we talk about scattering in the forward direction when it scatters in the forward direction only it can be shown it can be proved that the atomic scattering factor will be equal to the atomic number; that means, the total number of electrons in the atom multiplied by the amplitude scattered by an electron whole thing divided by the amplitude scattered by electron.

So, f becomes simple is equal to z. So, if we consider a uranium atom. So, when x with 92 extra nuclear electrons then when an extra beam falls on those electrons and we consider scattering in the forward direction only small f or atomic scattering factor is equal to 92. If on the other hand we have a hydrogen atom then what will happen hydrogen has got one extra nuclear electron then if you have a beam of X-rays falling on an atom of hydrogen. So, it will scatter radiations in forward direction. So, for that hydrogen atom f is simply going to be 1.

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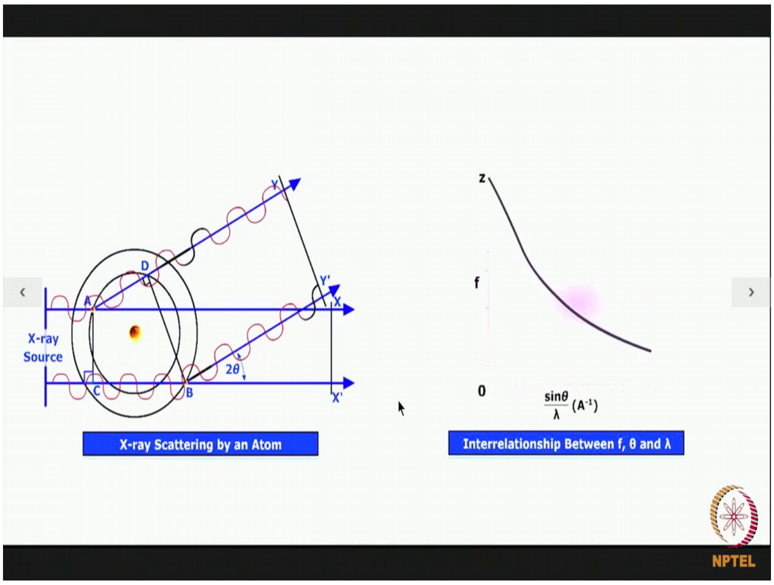

So, please remember that when the atomic scattering factor is equal to the atomic number we are talking about scattering in the forward direction only now what about the value of atomic scattering factor when we are considering scattering in directions other than the forward direction that is given by this plot. So, this is a plot of f versus sine theta by lambda. So, you see that this theta gives some idea of which direction we are measuring this scattered intensity and lambda is a wavelength of x radiation. So, what we find z varies in this fashion z varies in this fashion; I am sorry, f varies in this fashion and when theta is equal to 0 theta is equal to 0 means the forward direction then what happens we are over here.

So, when theta is equal to 0 we are at this origin and at this origin what is the value of f it is equal to z. So, you say that only forward direction if you consider this scattering then atomic scattering factor of an element is equal to its atomic number and when we consider scattering in any other direction that is the theta other than 0; you know you will find a atomic scattering factor is lower than in the case of scattering in the forward direction.

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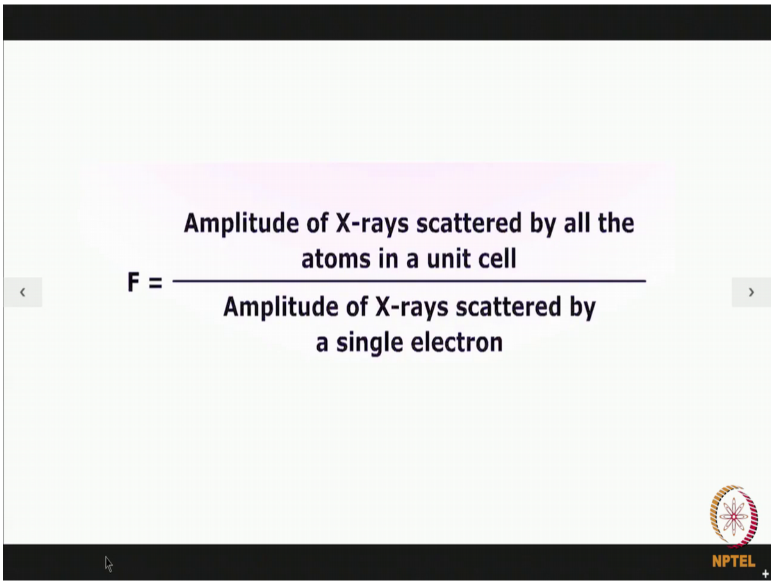

We will now talk about another very important factor and we call it the crystal structure factor we call it the crystal structure factor and denoted by capital F. So, by definition the crystal structure factor is equal to the amplitude of X-rays scattered by all the atoms in a unit cell of a material divided by the amplitude of X-rays scattered by a single electron.

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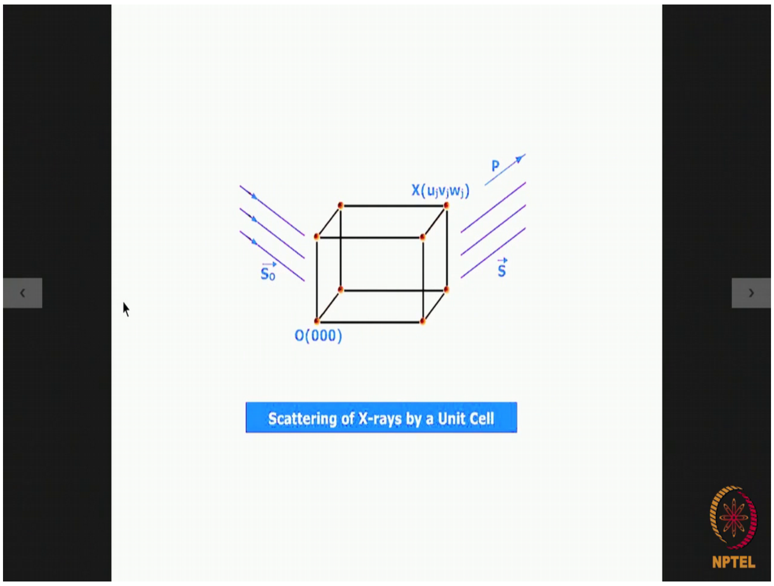

Say for example, this is a unit cell of a material and say a beam of X-rays is incident in this direction and the beam is designated by a unit vector S 0 as we did previously and say the scattering taking place in this direction we are interested to find out what is the scattered intensity in this direction this is denoted by scattered rays are denoted by the unit vector S.

Say for example, we have got an atom we are talking about an atom here which is our origin and an atom over there. So, we take this as the origin and say this is the j-th atom in the unit cell. So, we are first considering an atom at the origin this we have taken as a origin with fractional coordinates 0 0 0 and the j-th atom whose fractional coordinates are u j v j w j. Now we have already seen that when we calculate the scattered radiation from 2 different atoms.

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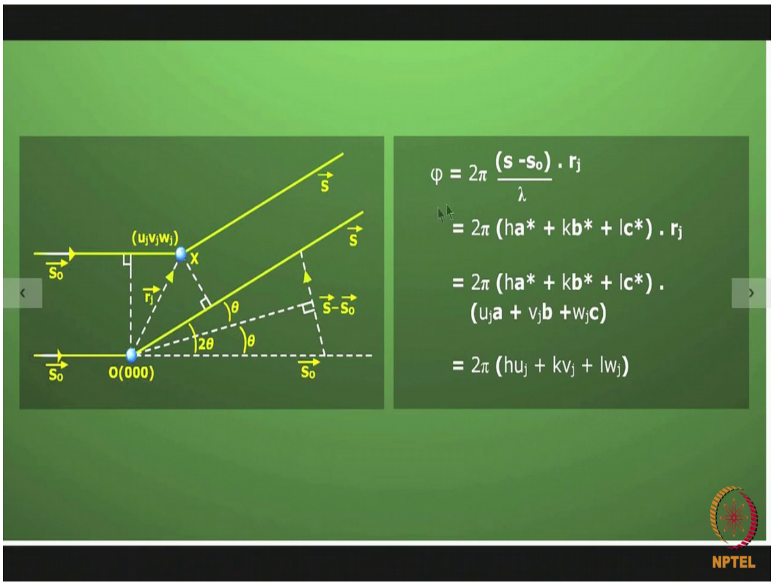

There is going to be a face difference between the 2 and that face difference can be simply written as equal to 2 pi times S minus S 0 by lambda dot r j where r j is this vector connecting the origin to the point to the atom at X. So, this relationship we derived previously. So, this is the face difference between the rays scattered by the atoms at this position and at this position.

Again we have seen that here if we take the s minus s 0 by lambda as the vector sigma star h k l in the reciprocal lattice we can write it simply as h a star plus k b star plus l c star and r j is nothing but u j a plus v j b plus w j c a b c are the lattice parameters say in the real space. So, it will be equal to 2 pi h u j plus k v j plus l w j.

So, if we have 2 atoms one at the position 0 0 0 in a unit cell and the other atom at the position u j v j w j then the phase difference between the rays scattered by the 2 atoms will be equal to 2 pi times h u j plus k v j plus l w j. Now you see whenever we are going to find out when we are going to add up this scattered waves from a number of atoms in the unit cell there should be a suitable method to add them up, because one thing is true that when we talk about the scattered radiation they have not only a magnitude but they have a phase difference also. So, it is a kind of vector addition of waves that we have to do.

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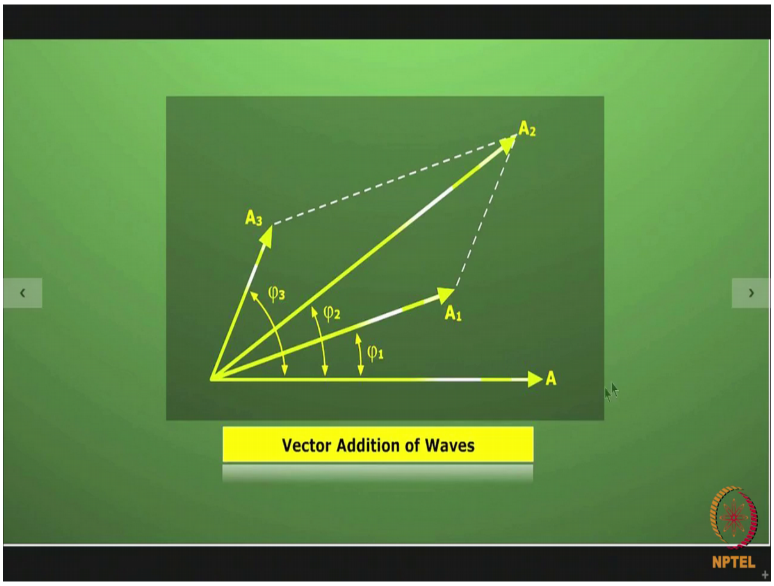

Say for example, we have got say 3 waves one giving by A 1, the second one given by A 2, third one given by A 3. Say with respect to a particular wave A 1 has got a phase difference with it by the amount phi 1 A 2 has got a phase difference with it by the amount phi 2 A 3 has a phase difference with it given by phi 3.

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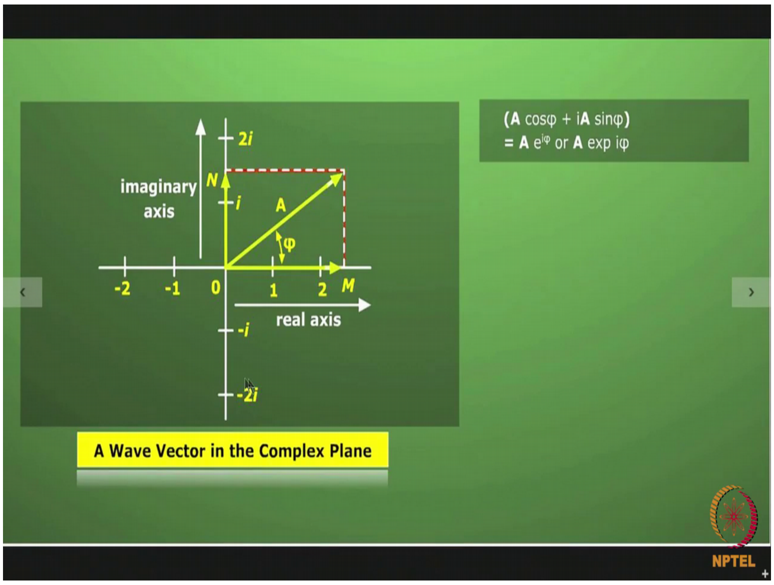

So, how to add up the scattered radiations from all the atoms in the unit cell? So, every scattered wave can be resolved into 2 components one along the real axis and the other along the imaginary axis. For example, if this vector makes a angle phi the real axis then we can write down this vector as a cosine phi plus I A sin phi. So, this quantity can be written either as A e to the power I phi or we can write it as a exponential I phi.

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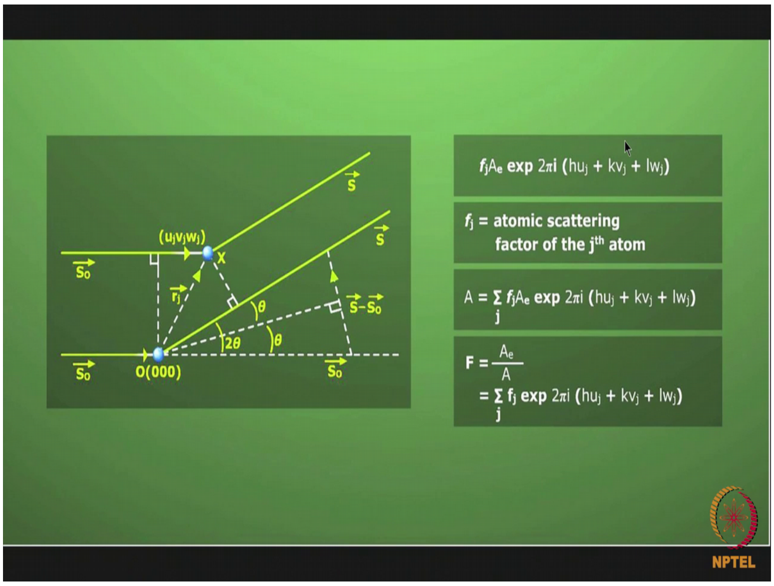

So, now what will be the amplitude of X-ray scattered by the j-th atom. We know that if f is the atomic scattering factor small f is atomic scattering factor.

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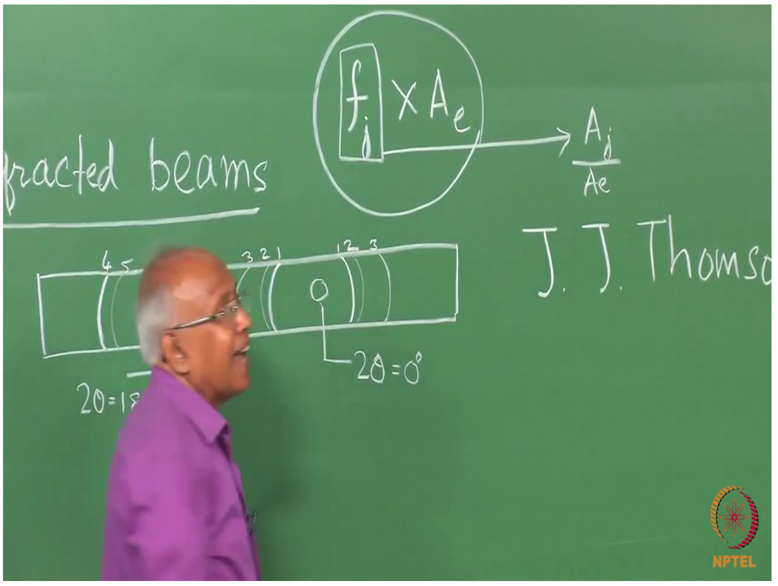

So, in this case f j is the atomic scattering factor of the j-th atom. So, if we multiply it by A e the amplitude scattered by single electron what it gives because, f j the atomic scattering factor is nothing but the amplitude scattered by the j-th atom divided by A e you see f j the atomic scattering factor of the j-th atom is nothing but the amplitude scattered by the j-th atom divided by A e amplitude scattered by single electron. So, if we multiply this with A e.

That means, it will give us the total amplitude scattered by the j-th atom. So, in this equation this is the total magnitude of the you know the total amplitude scattered by the j-th atom is f j multiplied by A e and this is the phase term. So, when we write down the total amplitude scattered by the j-th atom which will give you the value of the amplitude the magnitude of the amplitude and the phase term it will be f j A e multiplied by exponential 2 pi i into h u j plus k v j plus l w j.

So, this is the total amplitude scattered by the j-th atom in the unit cell now what will be the total amplitude which is scattered by all the atoms in the unit cell. So, this expression we take the summation of this over all the j atoms in the unit cell. So, knowing the amplitude scattered by the j-th atom as this we can easily find out what is the total amplitude scattered by all the atoms in the unit cell simply by having a summation of this quantity taken over all the j atoms. So, what will be the crystal structure factor f for the unit cell now here is a mistake it is written the reverse way. So, crystal structure factor will be a divided by A e please note that there is been a mistake here. So, crystal structure factor will be a divided by A e where a stands for the total amplitude scattered by all the atoms in the unit cell divided by the amplitude scattered by a single electron.

So, this is A. So, we divide it by A e. So, what will happen A e; A e will cross out. So, we will have this explanation for the crystal structure factor. So, the crystal structure factor of a unit cell of a material will be equal to f j exponential 2 pi i h u j plus k v j plus l w j with summation taken over all the j atoms in the unit cell. We will apply this concept of crystal structure factor in some particular cases to illustrate how important this factor is say- we talk about 3 brave lattices belonging to the cubic system one is the simple cubic the other is the face centred cubic or FCC.

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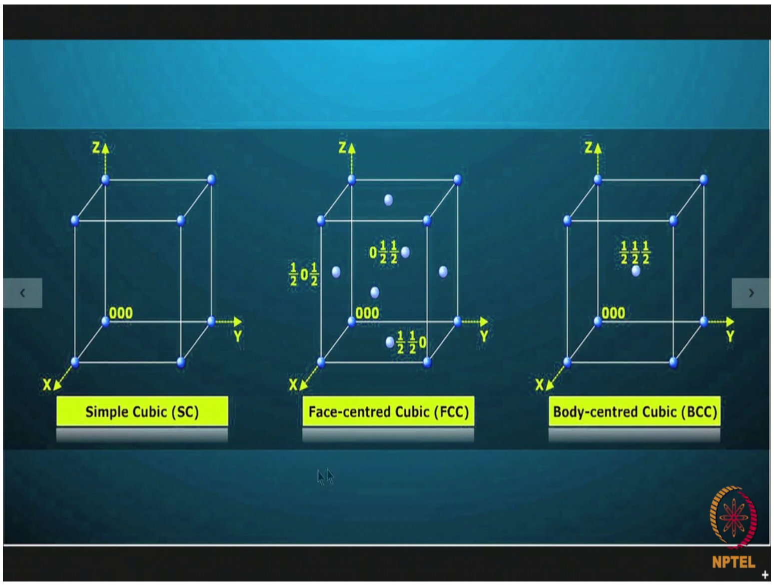

And the third one is the body centred cubic or BCC. Now you will remember that in simple cubic 8 corner atoms the total contribution to this particular unit cell is 1 atom here there are eight corner atoms and six face centred atoms. So, their total contribution to this particular unit cell is 4 atoms and in the body centred cubic the total contribution of the eight corner atoms and one body centred atom is just 2 atoms.

So, for as this particular unit cell is concerned. So, the 1 atom in the simple cubic system its fractional coordinates are 0 0 0 and the 4 atoms in the FCC unit cell have the fractional coordinates 0 0 0 half of 0 half 0 half and 0 half half and in the body centred cubic material the 2 atoms have the fractional coordinates 0 0 0 and half half half. Now let us talk about the simple cubic system how many atoms are there per unit cell there is only 1 atom at the origin 0 0 0. So, we have to take summation of that only 1 atom at 0 0 0.

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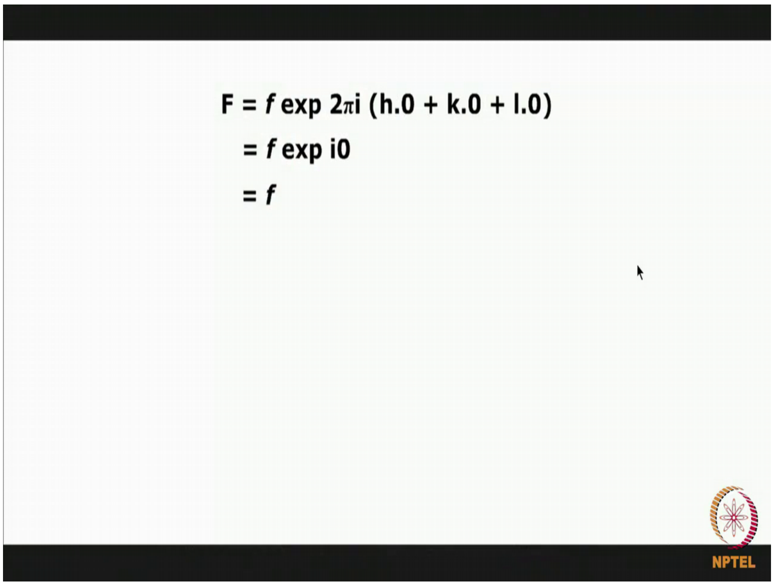

So, for simple cubic capital F is equal to small f exponential 2 pi i h into 0 plus k into 0 plus l into 0, so, how much it is small f exponential I into 0? So, it is equal to 1. So, it will be simply f. So, simple cubic system is one in which the crystal structure factor is simply equal to the atomic scattering factor.

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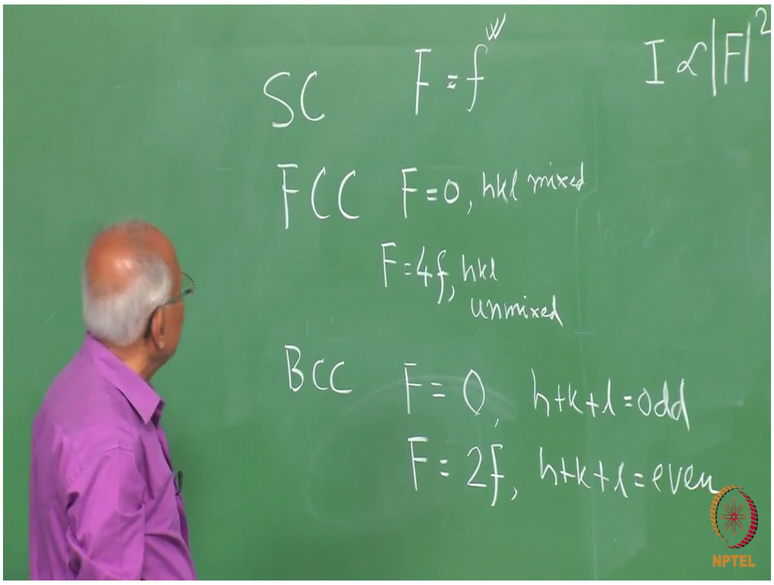

So, in the simple cubic system we find that capital F the crystal structure factor is simply equal to the atomic scattering factor assuming that the in the unit cell atoms are of the same kind now what does it say here we do not have any expression containing h k or l; that means, a simple cubic system crystal structure factor is independent of j k l. That means, you when you look at the amplitude the crystal structure factor it is the amplitude of x radiation scattered by all the atoms in the unit cell divided by the amplitude scattered by the single electron.

That means, in the when you consider the intensity of a diffraction line it is actually square of the amplitude. So, f square appears you know it is proportional to f square the intensity is proportional to f square. So, you see that f is the very important term in here and what it says in simple cubic it simply does not matter what are the h k l planes f is always a positive quantity you see small f is always a positive quantity small f is the atomic scattering factor and atoms will scatter you know depending on their atomic scattering factor.

So, there will be some intensity you know there will be diffraction possible from every h k l plane that is present in the material.

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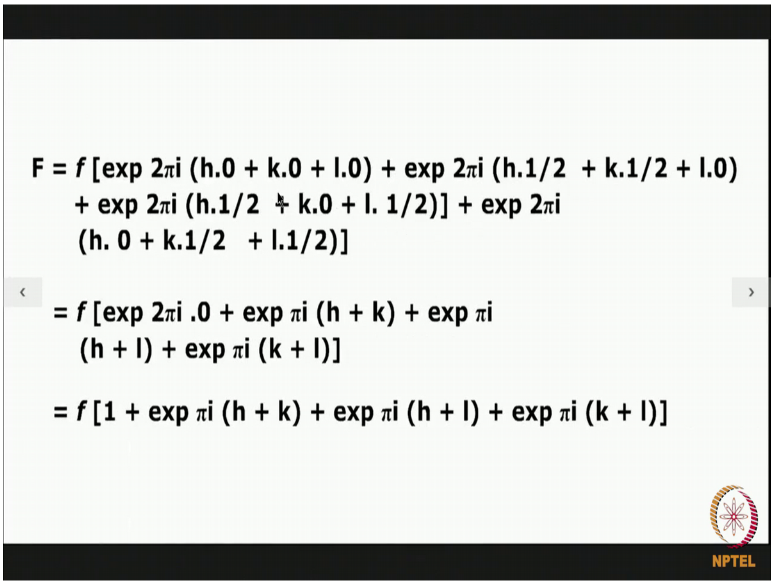

Now, let us got to the case of FCC the face centred cubic system now in FCC we know that there are 4 atoms per unit cell and they are located at the fractional coordinates 0 0 0 half half 0 0 half half and half 0 half. So, you see that when we calculate capital F; it has to be calculated over 4 atoms because in unit cell there are 4 atoms. So, we write down all those 4 terms f exponential 2 pi i h into 0 plus k into 0 plus l into 0 plus exponential 2 pi i h into half k into half plus l into 0 exponential 2 pi i h into half k into 0 l into half and exponential 2 pi i h into 0 plus k into half plus l into half.

So, that gives us equal to small f exponential 2 pi i into 0 plus exponential pi i h plus k exponential pi i h plus l exponential pi i k plus l. So, we have. So, this term is equal to 1 exponential 2 pi i into 0 is one. So, it is small f into 4 terms 1; 1 plus exponential pi i h plus k exponential pi i h plus l exponential pi i k plus l.

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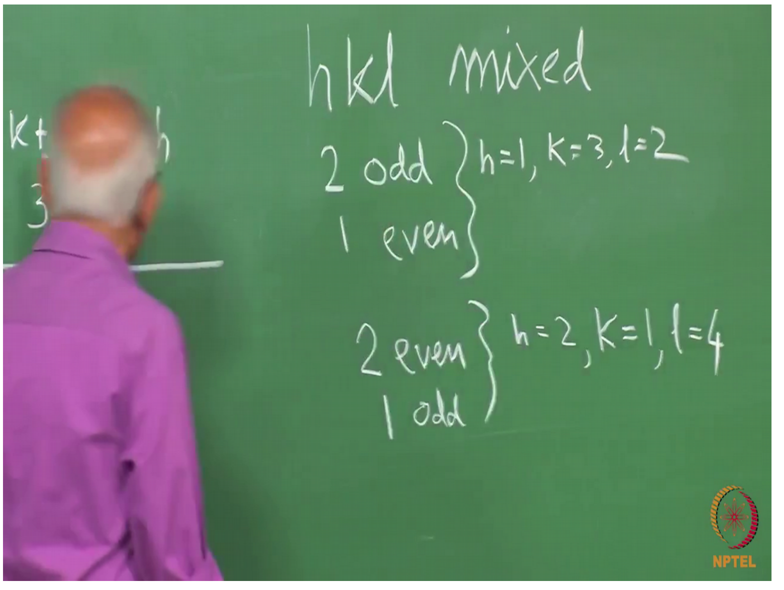

Now if we examine this expression very very carefully there can be some some different possibility. Say for example, if we have a situation where h k l are mixed quantities; that means, some are odd some are even then what happens if h k l are mixed quantities say 2 of them are odd one of them is even this is a possibility or 2 of them even one of them an odd quantity.

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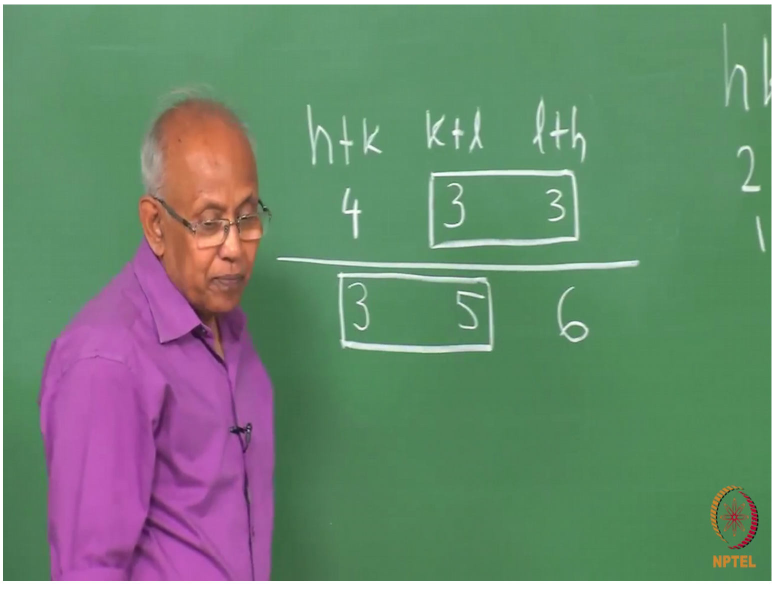

If that be the case what will happen to the values of h plus k; k plus l and l plus h say if it is this the 2 are odd one is even; that means, say for example, h k l we have h is equal to 2 k is equal to 4 2 odd. So, in this case, I am sorry.

So, in this case let us say that h is equal to 1 k is equal to 3 l is equal to 2. So, 2 odd and 1 even. So, what happens to these values h plus k is 4 k plus l is equal to 3 l plus h is equal to 3. So, we find one is an even quantity 2 are odd. Now let us look at the other possibility that out of h k l 2 are even say h is equal to 2 and 1 odd say k is equal to 1 and l is equal to 4.

Then what happens to these values h plus k will give us a value of 3 then k plus l will give us a value of 5 l plus h will us a value of 6. So, here 2 are odd one even and in this case also 2 are odd one is even. So, in these expression out of the 3 quantities h plus k h plus l k plus l say this is even this is even this is I am sorry this is odd this is odd this is even. So, 2 will be having odd values and one will be even value now we all know that exponential.

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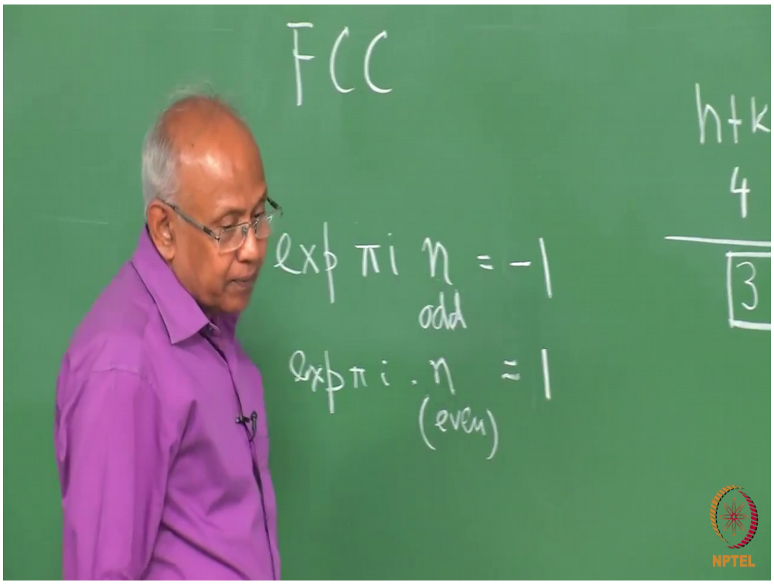

When you talk about exponential pi i into n when n is an odd quantity when n is odd this value is equal to 0 on the other hand exponential pi i into n where n is an even quantity it is equal to 1.

So, what will happen here; here out of this free expressions 2 will be minus 1 I am sorry I it was a mistake I made here I want to correct it. So, if it is odd quantity this has got a value minus 1 and if it is an even quantity it has got a value of plus 1. So, what will happen in these 3 expressions here 2 will be minus 1 1 will be plus 1.

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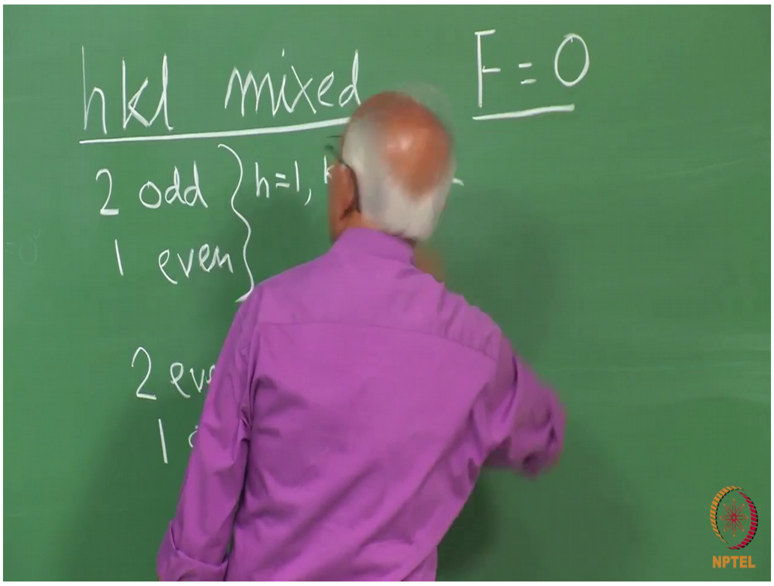

So, if we add them up it will be small f 1 minus 1 minus 1 plus 1; that means f into 0. So, it will be simply 0. So, you say that if we have a situation where h k l are mixed quantities then the value of f will be equal to 0 in case of FCC material. So, if we have an FCC material.

Then capital F will become 0 when h k l are mixed quantities. Now what is the other possibility that h k l are mixed quantities.

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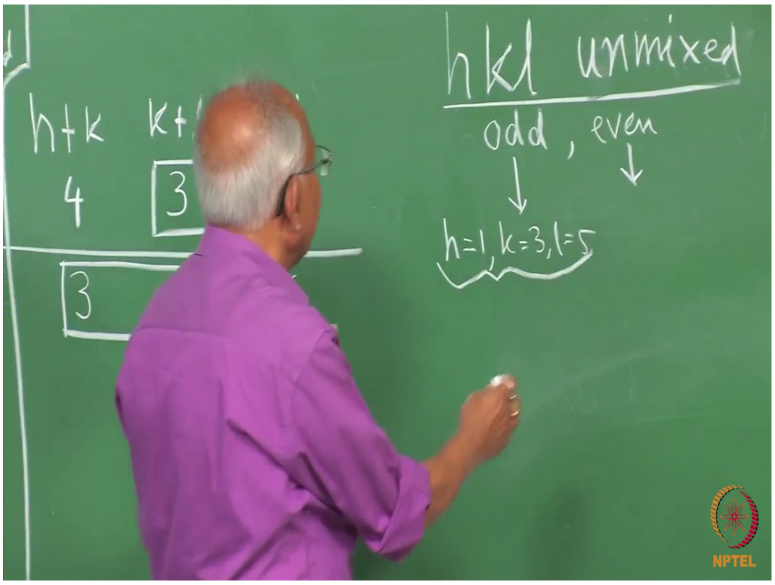

So, let us take a case where h k l are unmixed; that means, either all odd or all even. So, now, let us think about the possibility where h k l are unmixed which means all 3 of them are odd quantities or all 3 of them are even quantities.

So, when all 3 of them are odd quantities let us have h is equal to say 1 k is equal to 3 l is equal to 5 all odd quantities. So, what happens to h plus k it is an even quantity k plus l that is also an even quantity l plus h that is also an even quantity. So, in that case we find that all these h plus k h plus l k plus l is an even quantity. Now and if all the 3 are even then of course h k l you know h plus k plus k plus l plus l plus h all are even quantity and if these are even quantities their values are 1 1 and 1.

So, we say that when h k l are unmixed quantities whether all of them are odd or all of them are even the 3 terms in this expression each one of them becomes equal to 1. So, as a result capital F becomes small f multiplied by four. So, here f becomes equal to 4 times small f when h k l are unmixed quantities. So, you see the implication of these results in case of simple cubic f is independent of h k l. So, any since small f is always a positive quantity because every atom will scatter then every atomic plane will be able to scatter the radiation.

What about FCC we find there will be no scattering when h k l are mixed quantities you see now we are talking about a unit cell. So, all the atoms of the unit cell is scattered and this is the situation where the scatter will be totally destructive and the total scatter intensity will simply be equal to 0 when we have h k l mixed. So, if you take a diffraction pattern of an FCC material h k l mixed those planes will not give raise to any diffraction.

On the other hand if you have h k l unmixed; that means, atomic planes for which the h k l values are unmixed quantities there will be diffraction, because capital F is equal to 4 f which is a positive quantity and intensity square of f like that. So, we say that compared to a simple cubic and comparing simple cubic at FCC simple cubic material will show more number of diffraction lines because all the h k l planes of different types can diffract, but here the number of diffraction lines will be less, because those planes for which h k l are mixed they will not be able to diffract.

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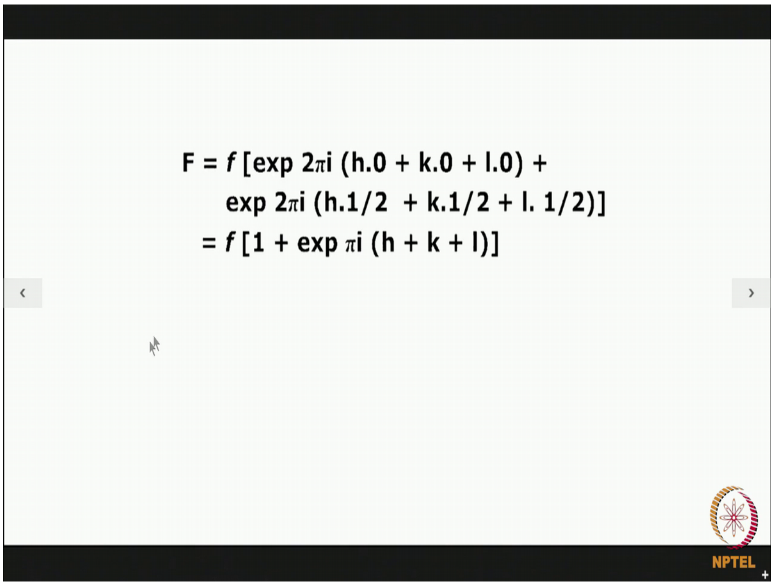

Now, we will go to the BCC case the body centred cubic unit cell. So, in the body centred cubic unit cell we know that there are 2 atoms per unit cell one located at diffractional coordinate at 0 0 0 the other located at half half half position. So, the summation here has to be taken over 2 atoms only. So, it will be exponential 2 pi i h into

0 plus k into 0 plus l into 0 plus exponential 2 pi i h into half plus k into half plus l into half. So, it will be equal to small f into one plus exponential pi i h plus k plus l.

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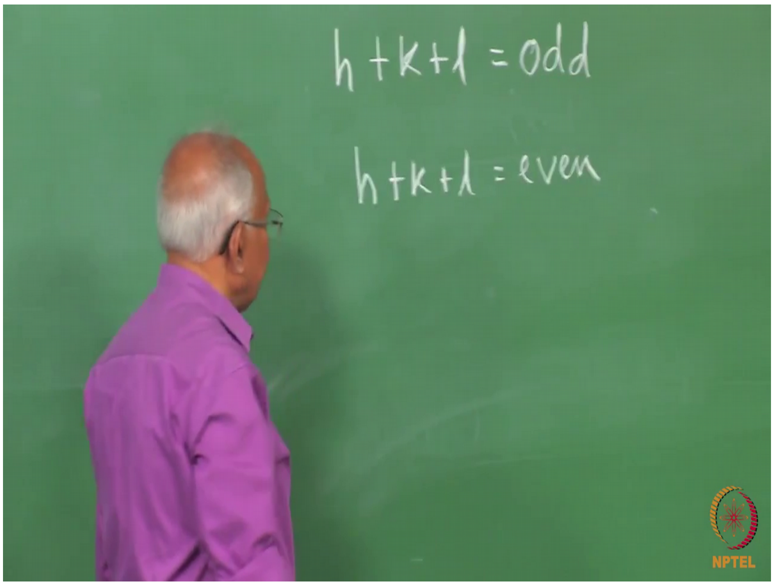

Now here again we can have 2 different possibilities say if h plus k plus l is equal to odd that is one possibility h plus k plus l is equal to even that is the other possibility now if h plus k plus l is odd then exponential pi i into h plus k plus l its value will be minus 1 and when h plus k plus l is equal to even the value of this quantity will be plus 1.

So, you say that here f will be equal to 0 when h plus k plus l is equal to and odd quantity when it is odd quantity this expression has got the value of minus 1. So, capital F will be small f into 1 minus 1 is equal to 0.

Now, how much will be f when h plus k plus l is an even quantity it will be one plus 1. So, it will be 2 f, when h plus k plus l is equal to an even quantity. So, you say that depending on the brave lattice and the location of the atoms we can have a positive atomic crystal structure factor in case of the simple cubic system for all atomic planes and we are we have already said that when we talk about the intensity; intensity is always proportional to the square of the amplitude of the x radiation which will be scattered by all the atoms in the unit cell.

So, in simple cubic system all the atomic planes will be able to diffract in case of FCC only those atomic planes for which h k l are unmixed will be able to diffract and in case of BCC materials only. In those cases where h plus k plus l is an even quantity will be able to diffract.