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Lecture-26
Materials Characterization
Fundamentals of X-ray diffreaction

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Hello everyone welcome to this material characterization course in the last class we looked at the x-ray diffraction conditions through blobby equations and we compared that blobby 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 items in the planes whereas in the lower conditions we were able to obtain the diffraction conditions for the rows and net as well as the three-dimensional addresses.

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 are demonstrated how this evolves 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 so look at this first slide.

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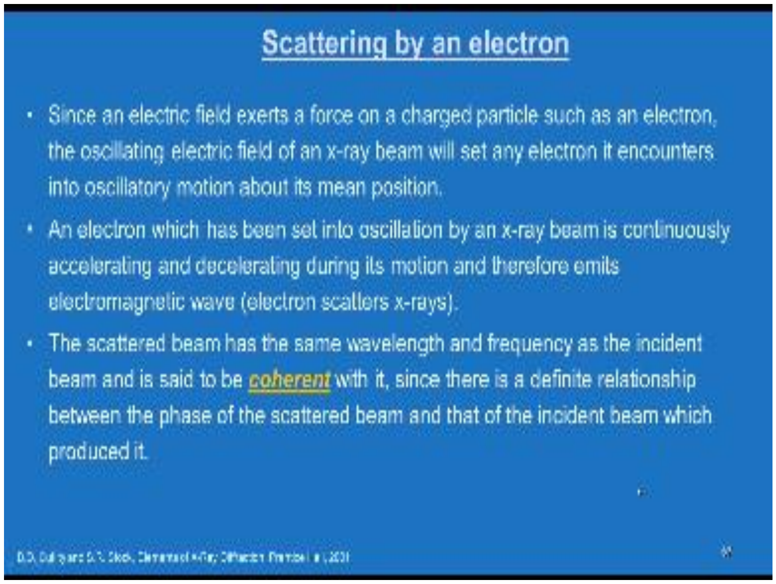

Where some of the important remarks about scattering by an electron x-ray scattering by an electron, since an electric field accepts a force on a charged particle such as an electron the oscillating electric field of an x-ray beam will set any electron it encounters into oscillatory motion abort its 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 scatter 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 face 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.

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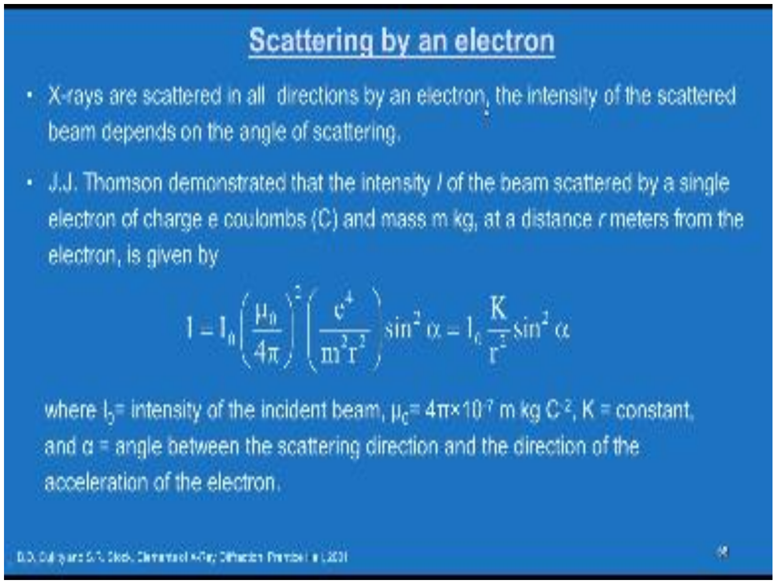

X-rays are scattered in all directions by an electron the intensity of the scattered beam depends on the angle of scattering. J.J. Thomson demonstrated that the intensity I of the beam scattered by a single electron of charge e columns and the mass m in kg at a distance r meters from the electron is given by $I=I_0(\mu_0/4\pi)^2(e^4/m^2r^2)\sin^2\alpha$ which is equal to $I_0K/r^2 \sin^2\alpha$ where I_0 is the intensity of the incident beam u_0 is equal to $4\pi x10^{-7}$ mkg/C2, K= constant and α angle between the scattering direction and the direction of the acceleration of the electron.

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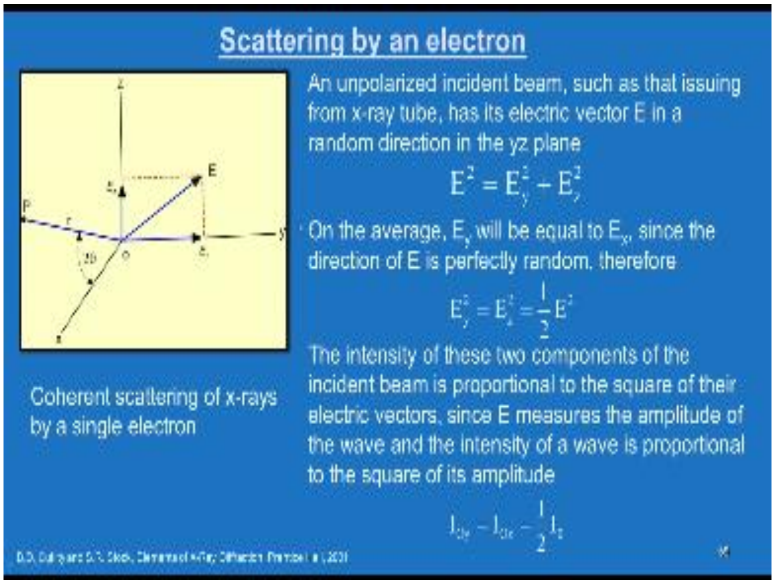

Suppose if you look at this kind of coherent scattering of x-ray by a single electron assuming that this is the coordinate where you have all this electric vectors in the mutual perpendicular direction X Y Z and then we can try to account for the intensity of the x-rays scattered by an electron, so look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

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 Ioy-Ioz=1/2I_0 with respect to this schematic.

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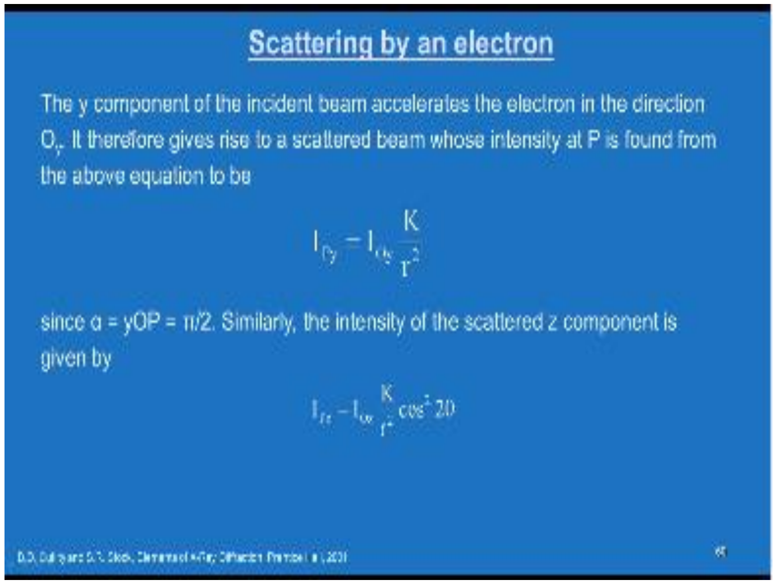

The y component of the incident beam accelerate the electron in the direction oh why it therefore gives rise to a scattered be whose intensity at P is found from the equation to be IPy=Ioy times K/r^2 since α=yoP which is equal to π/2 similarly the intensity of the scattered z component is given by IEz=IOz times K/r^2 $\cos^2 2\theta$.

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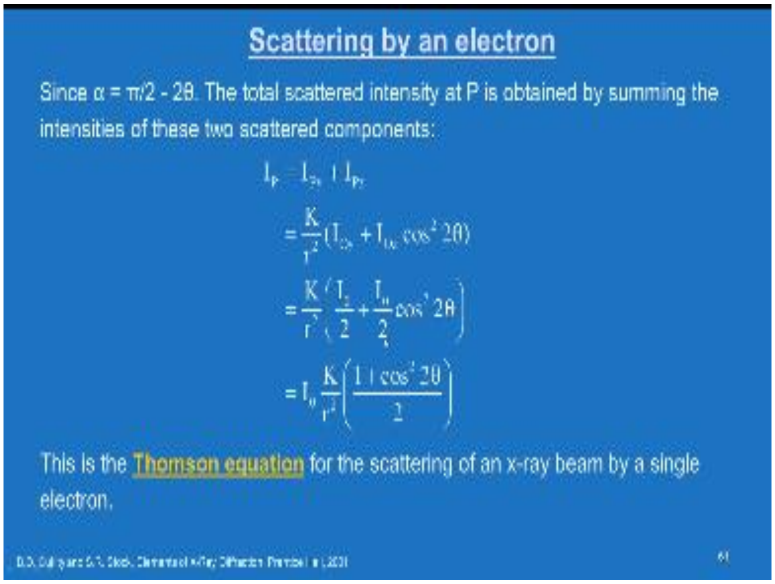

And we can look at the other expressions since $\alpha=\pi/2-2\theta$ the total scattered intensity at P is obtained by summing the intensity of these two scattered components Ip=Ipy+Ipz which we can substitute in this form $K/r^2(Ioz\ cos^2 2\theta)$ and then we can rearrange them into I_0 not into $K/r^2(1+cos^2 2\theta/2)$ this is the Thomson equation for the scattering of an x-ray beam by a single electron.

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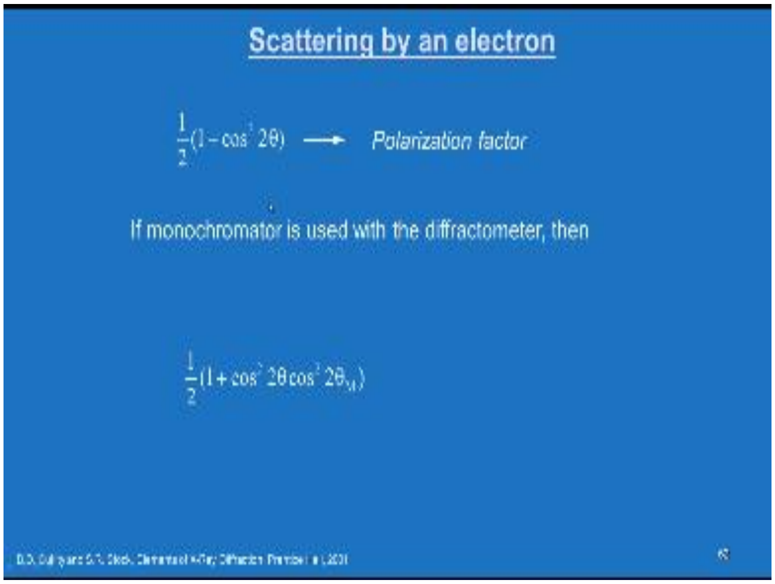

Where ½$(1+\cos^2 2\theta)$ is called a polarization factor which we will be incorporating in all the intensity equation whenever we are going to write if monochromator is used with the diffractometer then this expression is modified into this form that is ½$(1+\cos^2 2\theta\cos^2 2\theta m)$.

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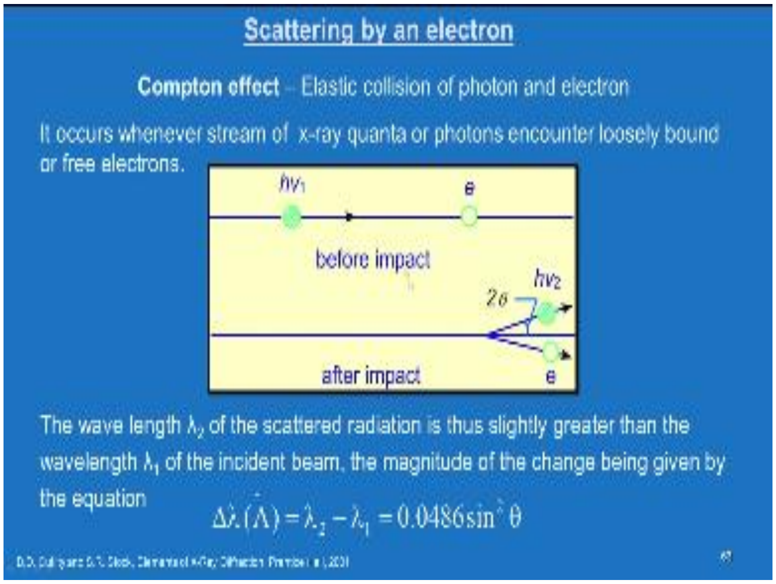

Now we will look at another form of scattering which is called a Compton effect which describes the elastic collision of photon and electron. It occurs when the stream of x-ray quanta are photons encounters loosely bound or free electrons, so there is a slightly different from what scattering which we talked about previously and here it is the x-ray quanta we are talking about a 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 hv1 is colliding with an electron before impact like this then after impact it goes like this into two different directions.

The wavelength λ2 of the scattered radiation is the slightly greater than the wavelength λ1 of the incident beam the magnitude of the change being given by the equation Δλ which is non strong unit is equal to $\lambda 2-\lambda 1=0.0486\sin^2\theta$.

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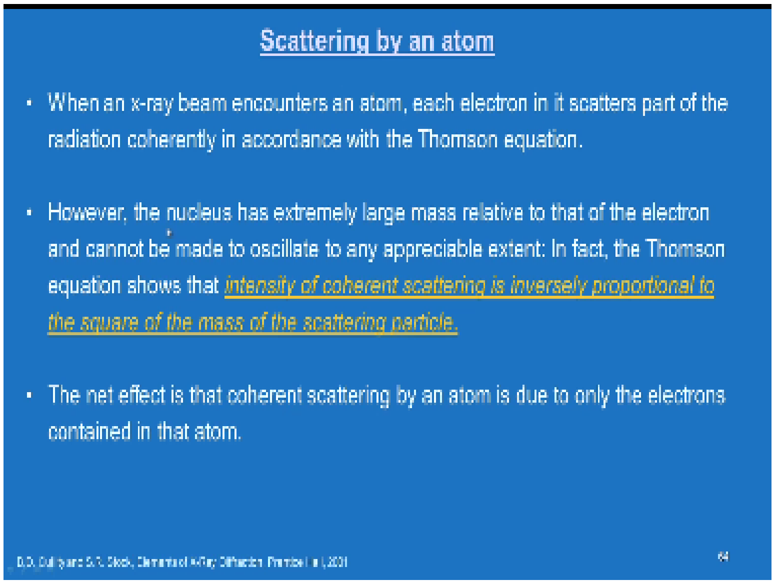

So when an x-ray beam encounters an atom each electron in it scatters part of the radiation coherently in accordance with the Thomson equation. However the nucleus has extremely large mass relative to the dolphin electron and cannot be made to oscillate to any appropriate extent in fact the Thomson equation 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.

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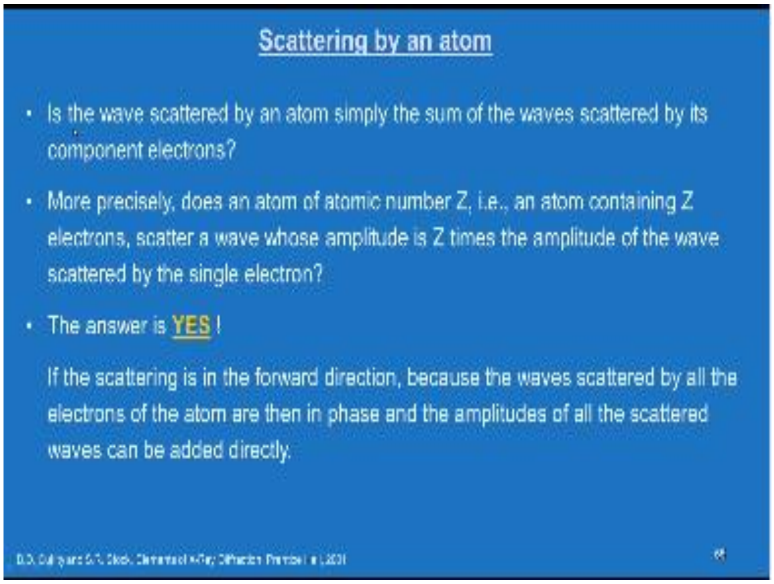

So now we have to ask some questions is the wave scattered by an atom simply the sum of the wave scattered by its component electrons more precisely does an atom of an atomic number z that is an atom containing Z electrons scatter a wave whose amplitude is Z times the amplitude of the wave scattered 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 or 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 devoted 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 can atoms.

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.

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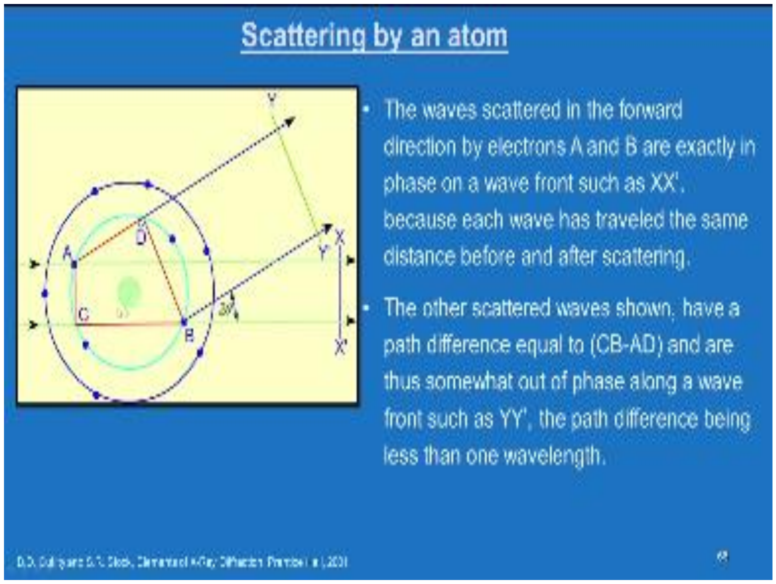

So look at this schematic this is a nucleus and you have the electrons in the orbits and then you look at this a green line where the forward scattering rays are shown and they are meeting this wave front X X′ and then you have the x-ray scattered in the other direction which are meeting in the YY wave 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 X X′ 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 first 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.

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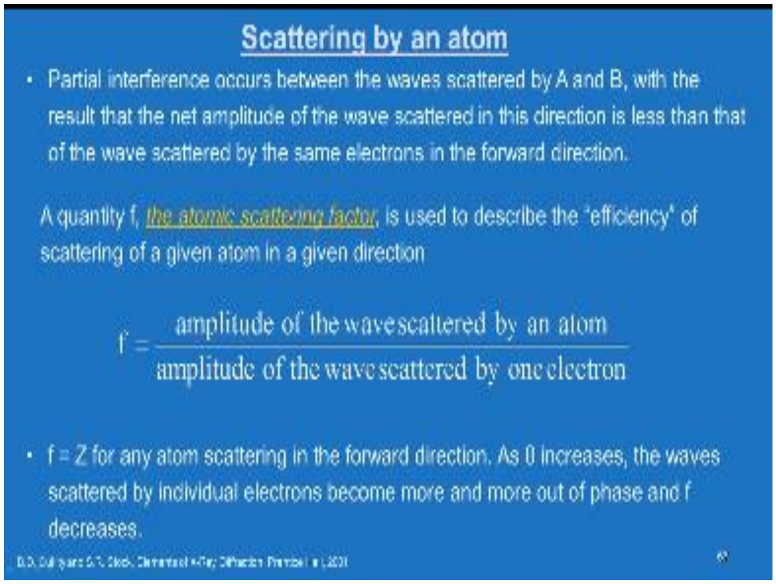

Only partial interference occurs between the waves scattered by A and B with the result that the net amplitude of the waves scattered in this direction is less than that of the wave scattered by the same electrons in the forward direction so this is the fundamental point we have to capture, so the waves 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 debt 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 our how about other rays which are contributing partially to the intensity.

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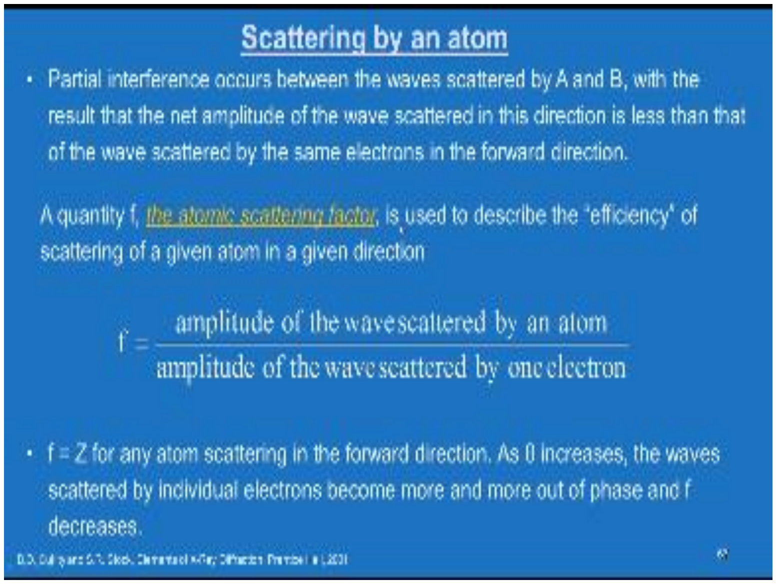

So a quantity of the atomic scattering factor is used to describe the efficiency of the scattering of a given atom in a given direction where F is equal to amplitude of the wave scattered by any atom by amplitude of the wave scattered by one electron. Suppose if F is equal to Z for any atom scattering in the forward direction as theta 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.

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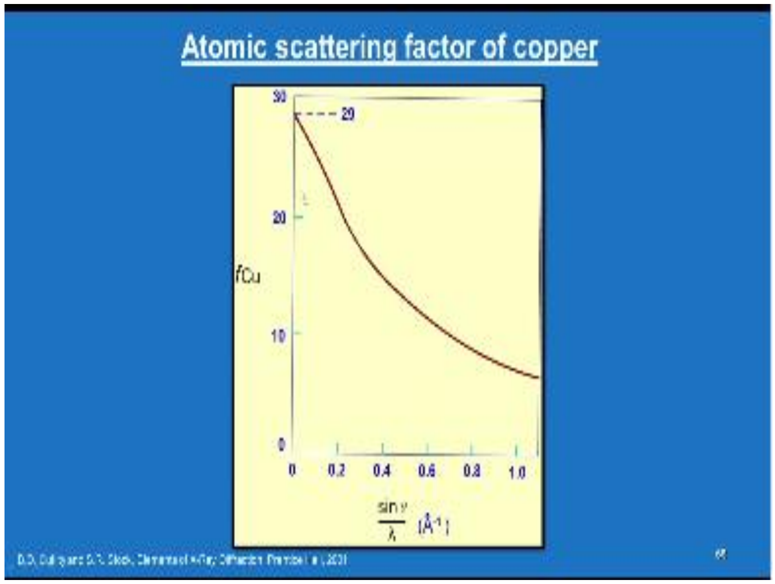

This is for the atomic scattering factor of copper where you see that as the η increases in fact it is not theta it is sinθ/λ which decreases as the θincreases you can see that atomic scattering factor also decreases so this is very important point.

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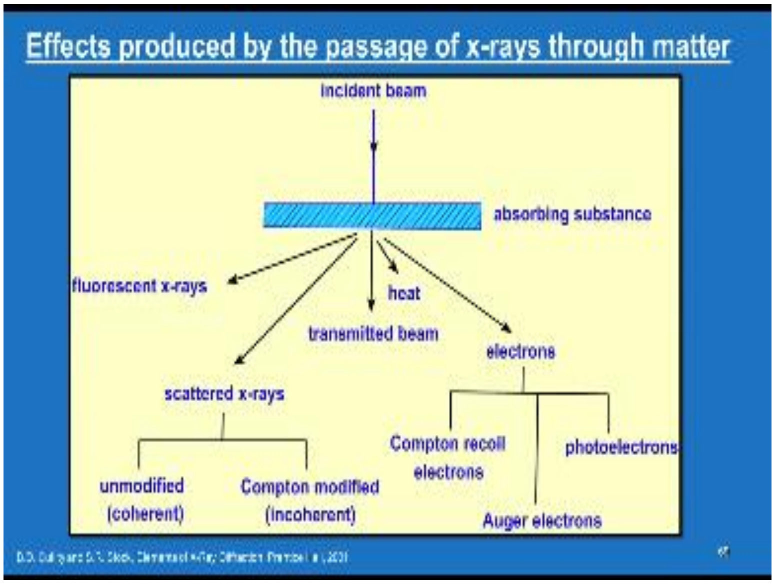

And now we will just look at the whole picture effects produced by the passage of x-rays through a matter in general you have the incident beam and this is your specimen absorbing some of the x-rays will be absorbed and some will release as a heat and then you have fluorescent x-rays coming out and then you have scattered x-rays and you have electrons coming out you have Compton recoil electrons and photoelectrons and OG 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.

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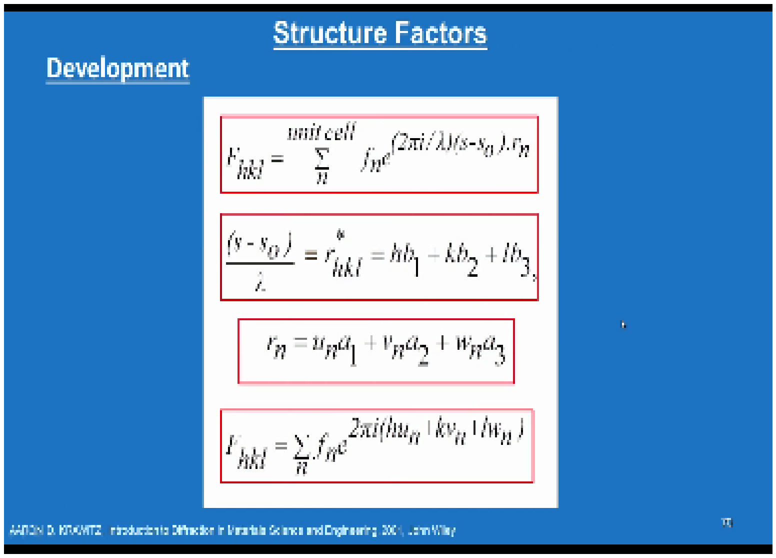

Now we will look at the structure factors we which is very important for the intensity calculations so the expressions which I have written all here all Mitch familiar to you the first one is the we have seen from the structure factor expression F_{hkl} is the atomic scattering factor from the all the 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.

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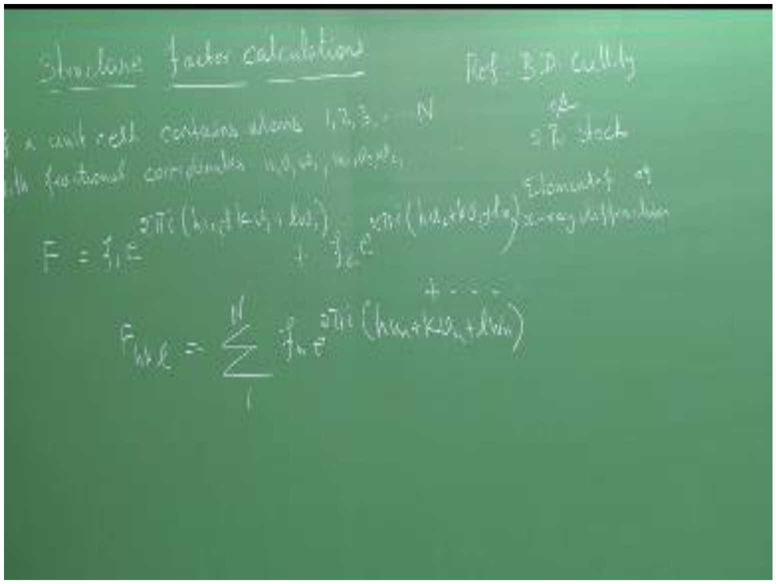

So I will go to the blackboard and then so what I have written is if a unit cell contains atoms 1 2 3 up to the N atoms with the fractional coordinates u1 v1 w1u2 v2 w2 extra then the atomic all the atomic scattering factors from that unit cell should be added like this and then if you sum it up and then that final equation appears like this so this is the summation of all the atomic scattering factors multiplied by $e^{2}\pi i(hu+kvn+lw)$ 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 are and I have taken this from this book BD quality and SR stock and you can go through for the entire a 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^{π} which is equal to e^{π} is equal to -1 and if it is $e^{2\pi i}$ an even number $e^{4\pi i}$Ior 6πI 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 eNπi is equal to -Nπi where N is any integer and you have this expression as well $e^{i\pi}+e^{i\pi}=2\cos x$.

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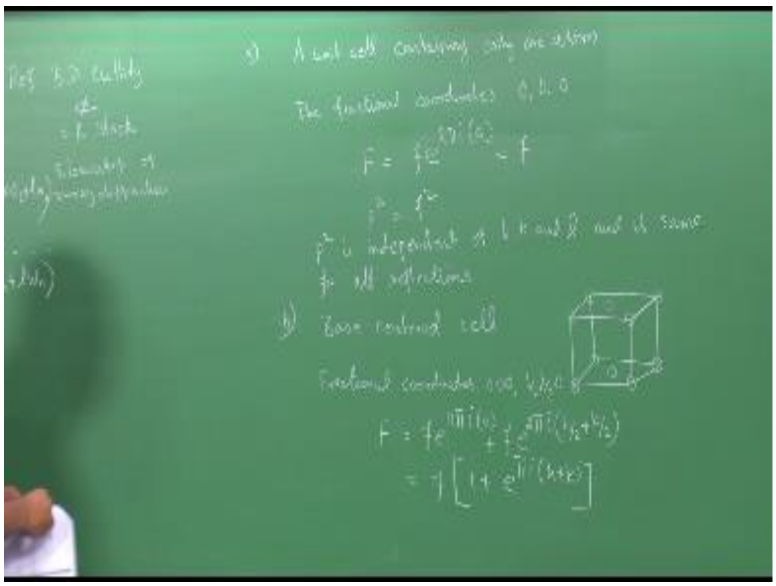

So now we will take up an individual expression I mean unit system unit cell containing only one atom so if you take up this expression the fractional coordinates 000 and the structure factor is $F=Fe^{2\pi i}$ which is equal to F and $F^2=F^2$, F^2 independent of so if you consider a unit cell containing only one atom then the fractional coordinates can be the origin one I mean 000 and then if you substitute that into this structure factor equation then you see that F is equal to $Fe^{2\pi i0}$ which is F because this component becomes 1 and then you get capital F is equal to 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 a 2 atoms per unit cell you is something like this a best centered unit cell and how do we calculate the structure factor the as usual we will start with the fractional coordinates means atoms located in the coordinates for this particular position s you have 000 and ½,1/2,0 these are the fractional coordinates you can see that 000 position this is ½,1/2,0 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 into 1plus $e^{\pi i}$ (h+K) so we will write something about this expression.

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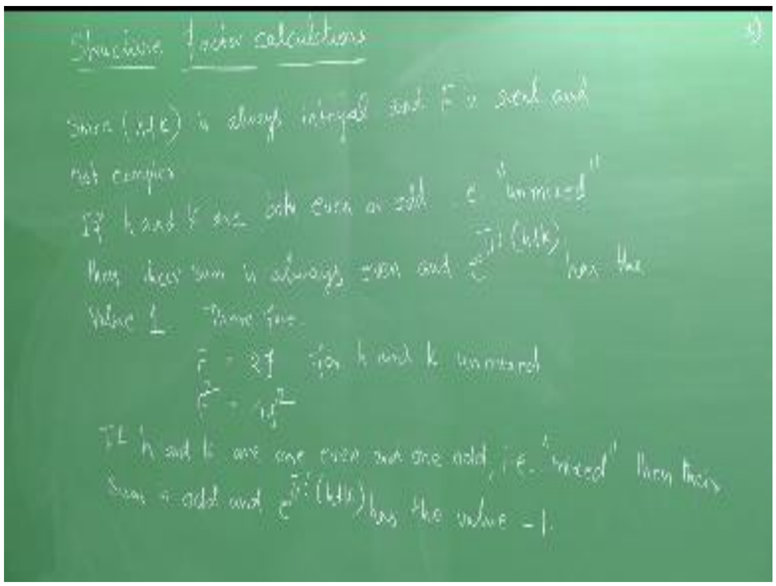

So this expression we may not be multiplied by the complex conjugate because h+K is always the integral and F is a real and not complex so this is the first step we have to understand and then what is the implication of this condition the implication is if h and K are both even are our that is unmixed indices then there some will always be an even. So the implication of this condition is if h and K are both even or odd that is unmixed then their sum is always even and you are $e^{\pi i}$ (h+K) has the value of 1 therefore you have F is equal to 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 some is odd and $e^{\pi i}$ (h+K) has the value of -1.

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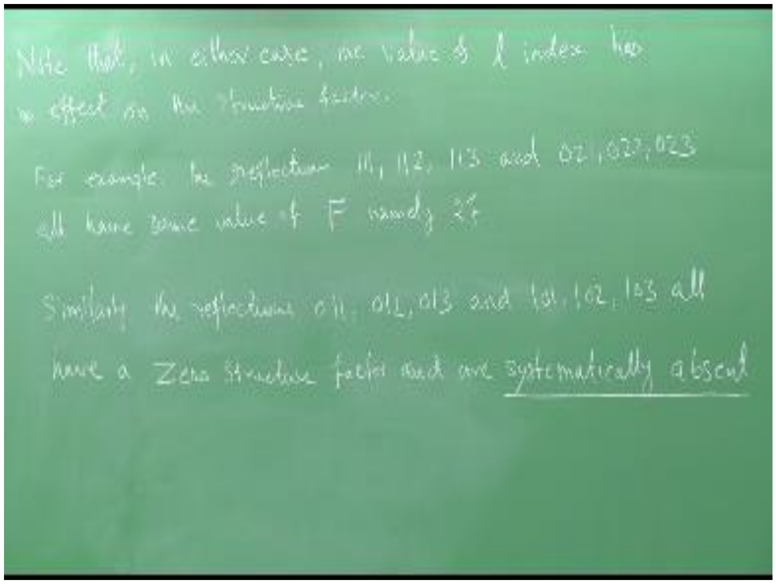

So this is the condition and we can now see that some of the indices what kind of reflection it will give. so if you apply this rule we can note that in either case the value of L index has no effect on the structure factor so that is what we are seeing here in both cases the indices L do not have any effect for example if we can take the reflections 111, 112, 113 and 0 to 1, 0 to2, 0 to 3 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 contribute 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.

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