Indian Institute of technology Madras
Presents

NPTEL
NATIONAL PROGRAMME ON TECHNOLOGY ENHANCED LEARNING

Lecture-27
Materials Characterization
Fundamentals of X- ray diffraction

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Hello everyone welcome to this material characterization course in last class we just looked at the x-ray scattering in terms of coherent and incoherent scattering and we found that a coherent scattering was explained by Thompson's equation and that incoherent scattering was explained by a Thompson effect and then we just try to understand the scattering of electron by x-rays and then we just moved on to the scattering by any unit cell and then we started looking at the structure factors and simple expressions basic expressions for the structures factors how we can calculate.

We started looking at a simple a unit cell where you have the one atom per unit cell and then we started looking at the structure factors for abase centered unit cell today we will continue this exercise and we look at some of the basic very important crystal systems like a body centered cubic lattice as well as a face centered cubic lattice and then we also look at some of the important crystal systems are ordered crystal systems like cesium chloride and sodium chloride and how this structure factor calculations are then.

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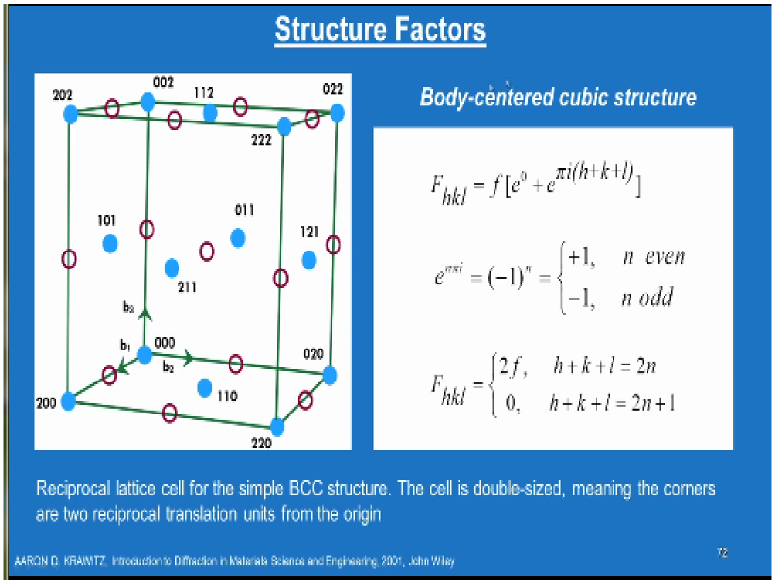

Structure Factors

Body-centered cubic structure

$$F_{hkl} = f\,[e^0 + e^{\pi i(h+k+l)}]$$

$$e^{n\pi i} = (-1)^n = \begin{cases} +1, & n \text{ even} \\ -1, & n \text{ odd} \end{cases}$$

$$F_{hkl} = \begin{cases} 2f, & h+k+l = 2n \\ 0, & h+k+l = 2n+1 \end{cases}$$

Reciprocal lattice cell for the simple BCC structure. The cell is double-sized, meaning the corners are two reciprocal translation units from the origin

AARON D. KRAWITZ, Introduction to Diffraction in Materials Science and Engineering, 2001, John Wiley

So me the first slide which I am trying to show here is the structure factor calculation for a body centered cubic structure and what you are seeing in the schematic here is not a body centered cubic structure but rather it is a reciprocal lattice cell for the simple BCC structure, so we will now try to understand this what we are seeing is a reciprocal lattice cell in fact we will try to understand this cell by looking into the structure factors in a neutral manner in a BCC cubic I mean the BCC structure.

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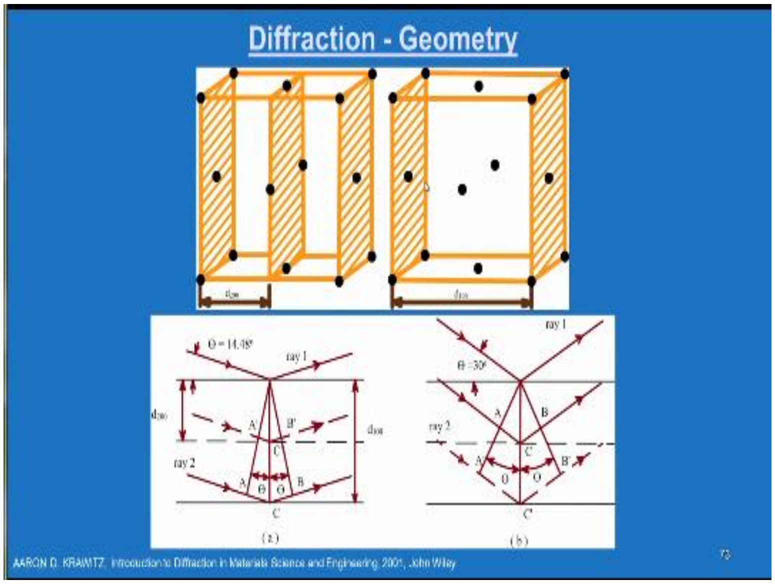

Diffraction - Geometry

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The structure factor can be written like this.

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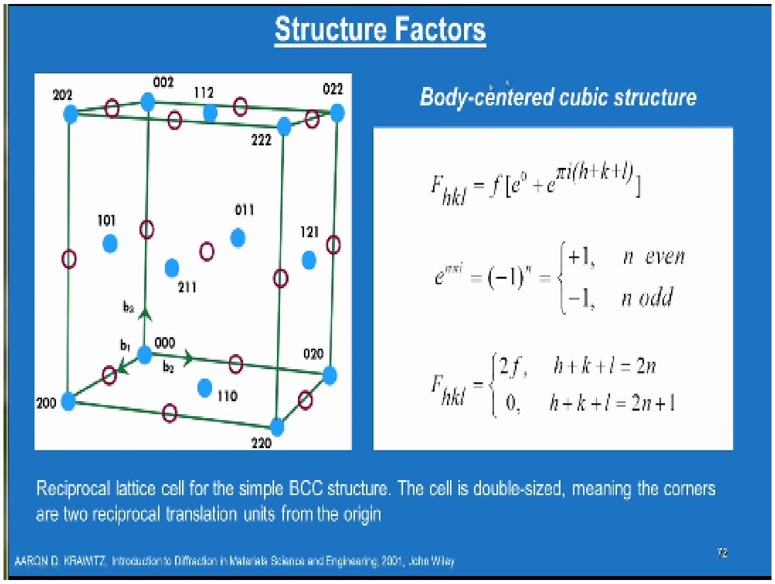

Structure Factors

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Reciprocal lattice cell for the simple BCC structure. The cell is double-sized, meaning the corners are two reciprocal translation units from the origin

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72

F_{hkl} is equal to f into e^0 to $+e^{\pi i}$ into h + k + l that means you have two atoms per unit cell one at origin one at the body center and then we have the complex exponential function will have the relation like this and if you for the BCC crystal structure the structure factor rules are F_{hkl} is equal to 2f f, h + k + l are equal to 2n if structure factor F_{hkl} is equal to zero if h + k + l is equal to 2n + 1 so that means we have to see whether this is true in this case what is reciprocal lattice here we will see the intensity only which are allowed reflections are seen here.

So what you are seeing here is it is the cell of double the size if you see that this is not 100 but 200 220 and 222 and 202 and so on, so what you have to appreciate is here is for a BCC simple BCC structure your reciprocal lattices and FCC unit cell in a reciprocal space and if you what are the hkl some is odd then you will see that they are all 0, for example you can see this all this other positions belong to this condition wherever you have this odd number, so like that you can verify the selection rule and then the structure factor from where you're going to get the intensity by looking at the reciprocal lattice.

We will see this the reciprocal lattice in an actual case when we look at the electron diffraction you will also appreciate what kind of direction and orientation we will get the spot and we will also see the forbidden positions in the reciprocal lattice cream, so like that we can look at some other system.

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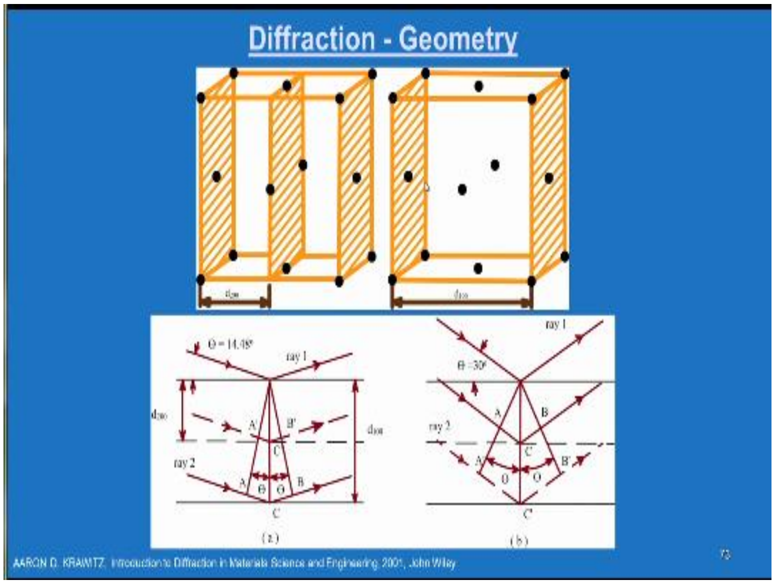

Diffraction - Geometry

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And before we look at the one more system let us also recall this problem we have already discussed but then just to give you a perspective of how the forbidden reflections are actually visualized in terms of some of the cubic system here in this case you have this FCC unit cell and then this is D 110 planes and then you also have D 200 planes and we have already discussed this how this the phase relations really cancel the sum of the intensities out of this reciprocal lattice and with respect to this diagram two diagrams that is A and B.

We will just now solve some simple problem to appreciate how the selection rules and the phase relations which whether it is add to the intensity or annual and cancel the intensity 20 so I would like to go to the blackboard and then solve this a simple problem regarding this simple bcc unit cell.

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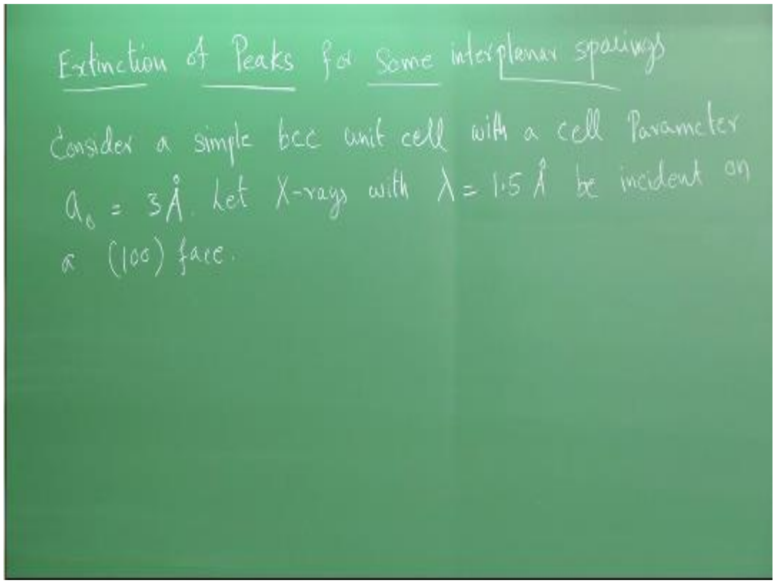

Extinction of Peaks for Some interplanar spacings

Consider a simple bcc unit cell with a cell Parameter $a_0 = 3Å$. Let X-rays with $\lambda = 1.5 Å$ be incident on a (100) face.

You so now we will look at the extreme extinction of a peaks for some interpreted spacing's in this case we take a BCC unit cell I consider a simple BCC unit cell with a cell parameter a_0 equal to 3Å let x rays with wavelengths λ which is equal to 1.5 Å be inserted on the 100 phase so now we will calculate the structure factor.

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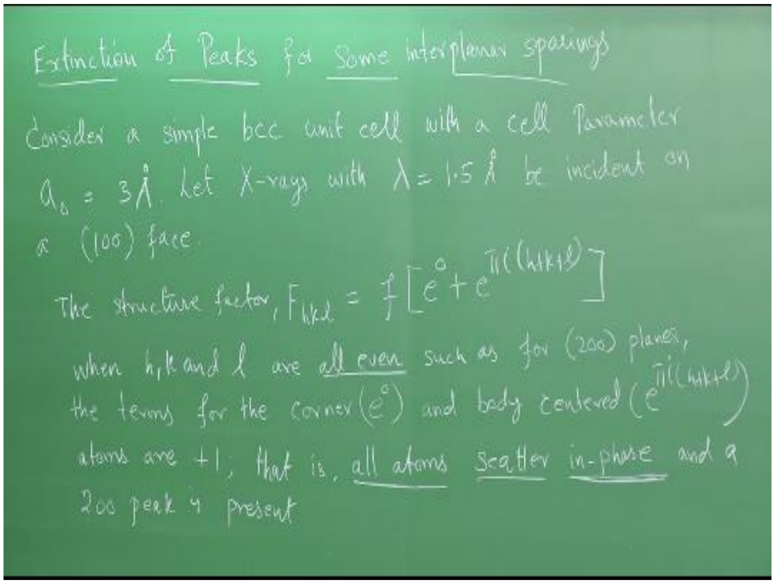

Extinction of Peaks for Some interplanar spacings

Consider a simple bcc unit cell with a cell Parameter $a_0 = 3Å$. Let X-rays with $\lambda = 1.5$ Å be incident on a (100) face.

The structure factor, $F_{hkl} = f\left[e^{0} + e^{\pi i(h+k+l)}\right]$

when h, k and l are all even such as for (200) planes, the terms for the corner (e^{0}) and body centered ($e^{\pi i(h+k+l)}$) atoms are +1; that is, all atoms scatter in-phase and a 200 peak is present

So this is the structure factor equation because of the two atoms per unit cell, so when hkl are all even such as for 200planes for example the terms for the corner atoms that is e^{0} and the body centered atom $e^{0\ \pi i\ (h +k + l)}$ atoms are + 1 that means what does that mean that means all atoms scatter in phase and a 200 peak is present, so according to this rule all atom scatters in phase so this things you have to remember and 200 peak is also present.

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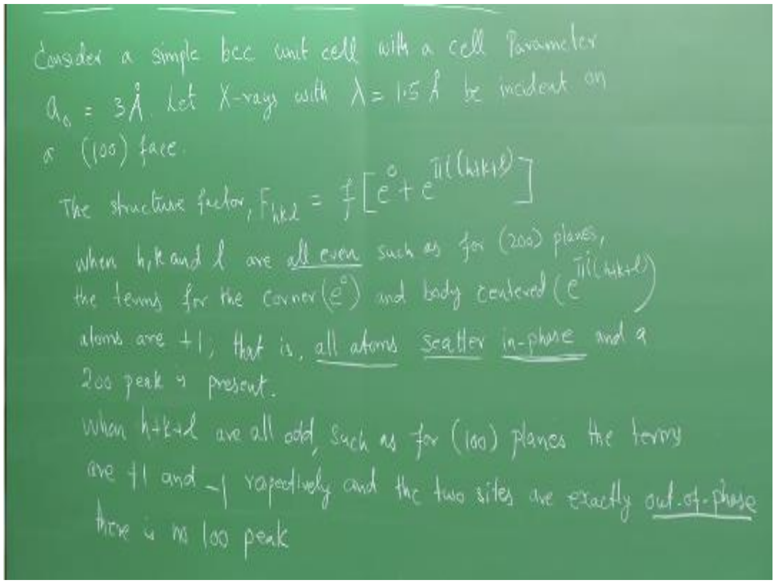

Consider a simple bcc unit cell with a cell Parameter
$a_0 = 3\mathring{A}$. Let X-rays with $\lambda = 1.5\,\mathring{A}$ be incident on
a (100) face.

The structure factor, $F_{hkl} = f\left[e^{0} + e^{\pi i(h+k+l)}\right]$

when h, k and l are <u>all even</u> such as for (200) planes,
the terms for the corner (e^{0}) and body centered ($e^{\pi i(h+k+l)}$)
atoms are +1, that is, <u>all atoms</u> <u>scatter</u> <u>in-phase</u> and a
200 peak is present.

When h+k+l are all odd, such as for (100) planes the terms
are +1 and −1 respectively and the two sites are exactly <u>out-of-phase</u>
there is no 100 peak

However when h + k + l are all odd such as 100 planes the terms are +1 and -1 respectively and the two sides exactly out of phase and there is no 100 so in fact what I have written is what I have shown in the slide in the previous slide where I showed the reciprocal lattice where you could see only these kind of planes not the this kind of pain because of this extinction rules.

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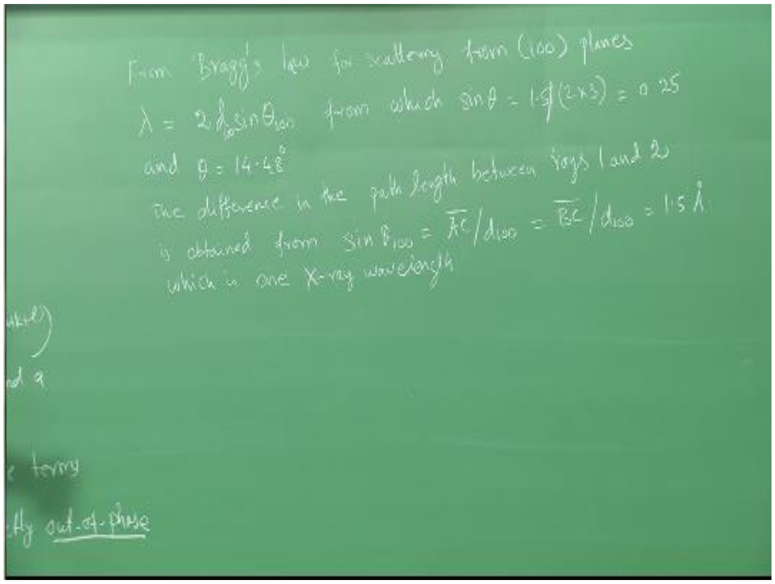

From Bragg's law for scattering from (100) planes

$\lambda = 2d_{100}\sin\theta_{100}$ from which $\sin\theta = 1.5/(2\times3) = 0.25$

and $\theta = 14.48^\circ$

The difference in the path length between rays 1 and 2

is obtained from $\sin\theta_{100} = \overline{AC}/d_{100} = \overline{BC}/d_{100} = 1.5$ Å

which is one X-ray wavelength

Now we can prove this concept geometrically we first solve Bragg's law for scattering from Bragg's law we can write for scattering 1 planes λ X equal to 2d 100 let us understand what we have done so far from the Bragg law for scattering from 100 planes you can simply write λ is equal to 2 d100 plane sine θ 100 from which we can find out the sine θ value sine θ is equal to1.5 divided by 2 into 3 which is equal to 0 point 2 5 correspond to the θ 14.4 a the difference in the path length between ray 1 and 2.

The of the Rays shown in the slide you can see that we can obtain it from sine θ 100 equal to AC / d 100 which is equal to BC/d_{100} which is equal to 1.5 Å which is one x-ray wavelengths. So that is what we have started with so it is one x-ray wavelengths.

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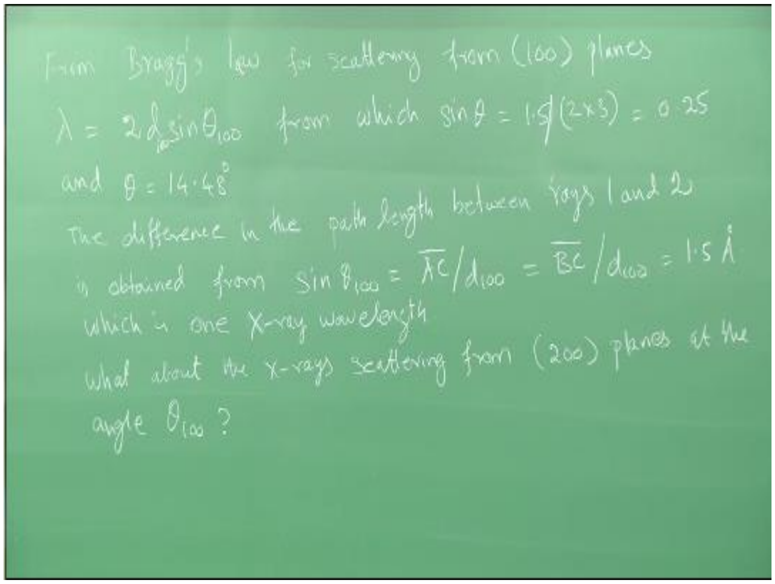

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and $\theta = 14.48^{\circ}$

The difference in the path length between rays 1 and 2

is obtained from $\sin\theta_{100} = \overline{AC}/d_{100} = \overline{BC}/d_{100} = 1.5\,\text{Å}$

which is one X-ray wavelength

What about the x-rays scattering from (200) planes at the angle θ_{100} ?

Now the question is what is what about the x-ray scattering from 200 planes at the angle θ100 so we can find out in a similar way.

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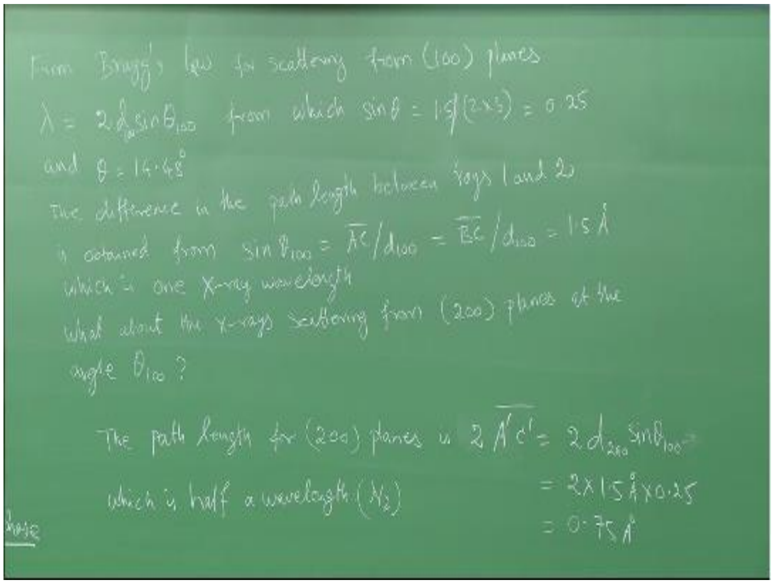

From Bragg's law for scattering from (100) planes

$\lambda = 2 d_{100} \sin\theta_{100}$ from which $\sin\theta = 1.5/(2\times3) = 0.25$

and $\theta = 14.48^\circ$

The difference in the path length between rays 1 and 2 is obtained from $\sin\theta_{100} = \overline{AC}/d_{100} = \overline{BC}/d_{100} = 1.5$ Å

which is one X-ray wavelength

What about the x-rays scattering from (200) planes at the angle θ_{100} ?

The path length for (200) planes is $2\overline{A'C'} = 2 d_{200} \sin\theta_{100}$

which is half a wavelength ($\lambda/2$)

$= 2 \times 1.5$ Å $\times 0.25$

$= 0.75$ Å

The path length, so the path length for 200 planes is two times A´ C´ it is equal to 2 d sine-θ 100 we can substitute this you will get point 7 5 Å as a path length which is off of the you so what is the consequence if you have the path length from 200 planes is exactly half the wavelength as we have discussed previously it will completely cancel out the intensity we can write that which will.

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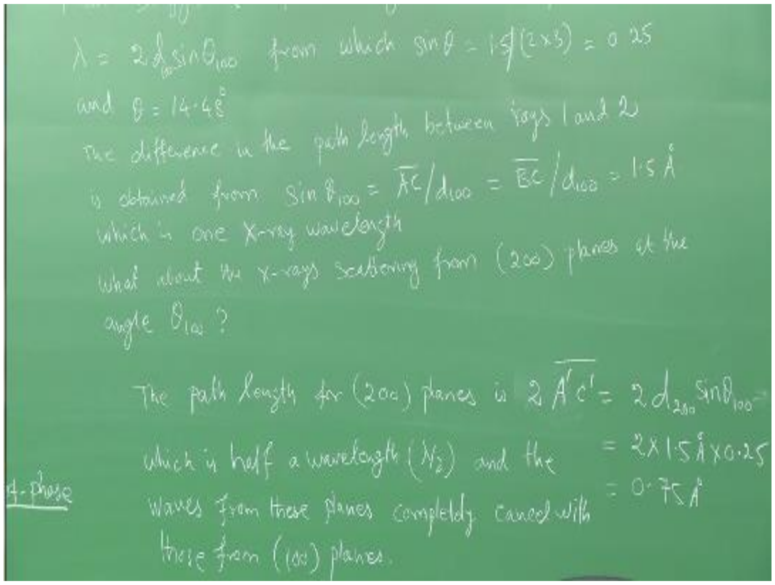

$\lambda = 2d_{100}\sin\theta_{100}$ from which $\sin\theta = 1.5/(2\times3) = 0.25$

and $\theta = 14.48^\circ$

The difference in the path length between rays 1 and 2 is obtained from $\sin\theta_{100} = \overline{AC}/d_{100} = \overline{BC}/d_{100} = 1.5\,\text{Å}$

which is one X-ray wavelength

What about the x-rays scattering from (200) planes at the angle θ_{100}?

The path length for (200) planes is $2\overline{A'C'} = 2d_{200}\sin\theta_{100}$

$= 2\times1.5\,\text{Å}\times0.25$

$= 0.75\,\text{Å}$

which is half a wavelength ($\lambda/2$) and the waves from these planes completely cancel with those from (100) planes.

t-phase

So when you have the path length for 200planes is as half a wavelength then the wave from these planes completely cancel with those from 100 planes that is why you do not see the peaks like 100 300and so on in that reciprocal that is now let us consider the scattering from.

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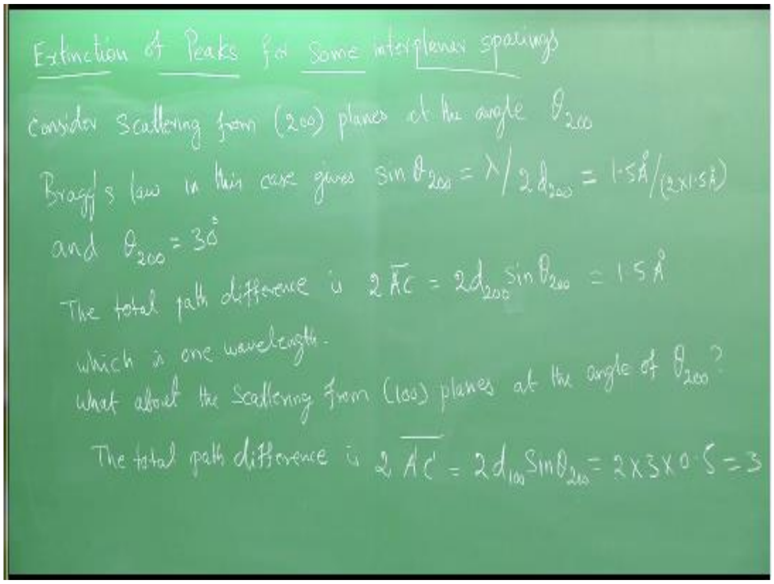

Extinction of Peaks for Some interplanar spacings

Consider Scattering from (200) planes at the angle θ_{200}

Bragg's law in this case gives $\sin\theta_{200} = \lambda / 2d_{200} = 1.5\text{Å}/(2\times1.5\text{Å})$

and $\theta_{200} = 30^\circ$

The total path difference is $2\overline{AC} = 2d_{200}\sin\theta_{200} = 1.5\text{Å}$

which is one wavelength.

What about the Scattering from (100) planes at the angle of θ_{200}?

The total path difference is $2\overline{A'C'} = 2d_{100}\sin\theta_{200} = 2\times3\times0.5 = 3$

So let us consider the scattering from200 planes at the angle θ 200 if you look at the slide the figure b shows this schematic excuse me and then we will now proceed with the calculations and the Bragg law for this case gives sine θ200 is equal to λ x $2d_{200}$which is nothing but 1.5Å / 2 x1.5Å which is worked out to θ 200 is 30 degree now at this angle the total path difference the total path difference is 2 times AC which is 2 d00 sine θ 200 which is nothing but 1.5 Å which is nothing but one wavelength.

Now similar question what we have asked there what about scattering from similar question here what about the scattering from 100 planes at the angle of θ 200 now then we can work it out this also the total path difference you so the total path difference in the case of scattering from 100 plane add angle of θ 200 is 2 times A ´C ´ is equal to $2d_{100}$ sine θ200 which is equal to 2 x 3 in 2.5 which is nothing but 3, 3 is 2 λ.

This value is nothing but 2 λ this is which is nothing but integral multiple of wavelength λ and supports the constructive interference process so from this example we have seen how this the 200 type of planes exist and what is the meaning of extinction of certain peaks in for some interpreter spacing in crystal in a cubic crystal like a BCC so these two examples give you some kind of an appreciation for this concept and now we will move on to the next example what I would like to show.

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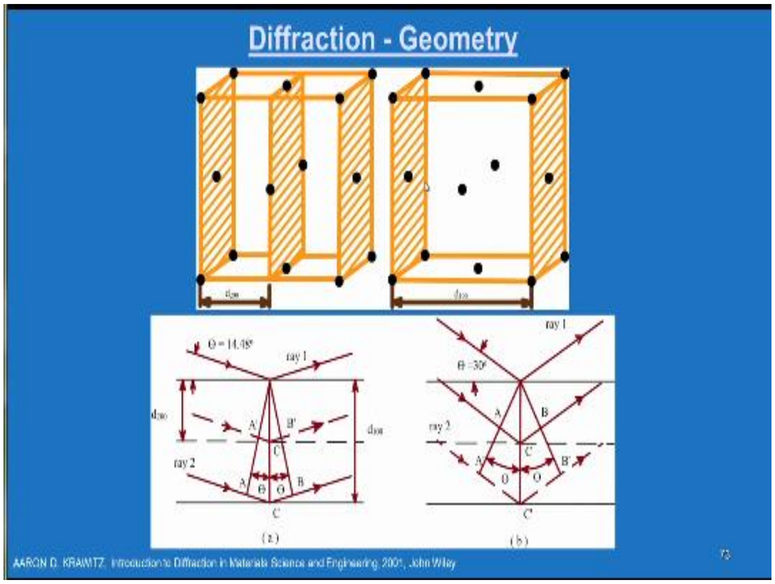

Diffraction - Geometry

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Come back to this slides.

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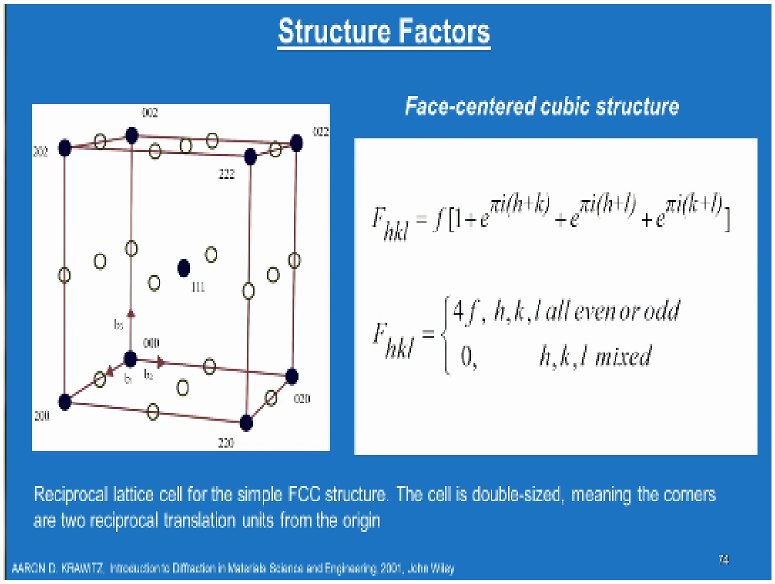

Structure Factors

Face-centered cubic structure

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

$$F_{hkl} = \begin{cases} 4f, & h,k,l \text{ all even or odd} \\ 0, & h,k,l \text{ mixed} \end{cases}$$

Reciprocal lattice cell for the simple FCC structure. The cell is double-sized, meaning the corners are two reciprocal translation units from the origin

AARON D. KRAWITZ, Introduction to Diffraction in Materials Science and Engineering 2001, John Wiley

If you look at this slide this is a structure factor calculation for a face centered cubic structure and if you write the expression you have four atoms per unit cell so you get the four terms here so $1+ e^{\pi i(h + k)} + e^{\pi i (h+ l)} + e^{\pi (k+ L)}$ so the rule is f, hkl is equal to 4 f where hkl or all even or odd and he the intensity will become outer structure factor will become0 when hkl are mixed so now you can see that this is again a reciprocal lattice cell so do not confuse this with a real self this is a reciprocal unit cells that means you will see the intensity spot actually in a double cell size and wherever you have the allowed reflection then only you will see the dark circles.

So here you can see that all hkl all even are all odd will have the allowed reflections so other positions are forbidden so what you can appreciate is the reciprocal unit cell for an Face lattice actually a BCC lattice and it is the same thing what we have seen before it is the other way around for an real BCC lattice the reciprocal lattices and FCC unit cell so that is clearly appreciated here.

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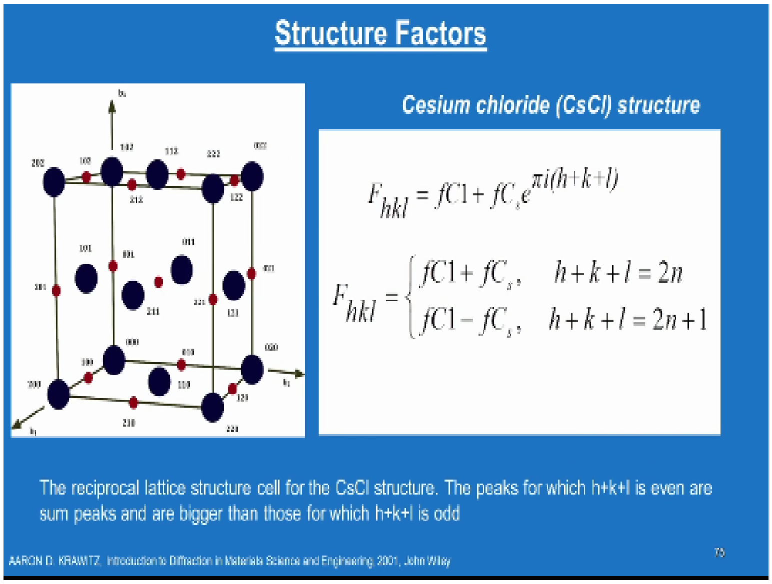

Structure Factors

Cesium chloride (CsCl) structure

$$F_{hkl} = fCl + fC_s e^{\pi i(h+k+l)}$$

$$F_{hkl} = \begin{cases} fCl + fC_s, & h+k+l = 2n \\ fCl - fC_s, & h+k+l = 2n+1 \end{cases}$$

The reciprocal lattice structure cell for the CsCl structure. The peaks for which h+k+l is even are sum peaks and are bigger than those for which h+k+l is odd

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Now we will see some interesting examples a cesium chloride structure where you have a cesium chloride type of structure you can see that it is kind of body centered unit cell has got two atoms that is chlorine and cesium atoms per unit cell which is one in corner another is in the body centered position but you can write the expression in terms of the structure factor equations like this and the selection rule is you see if hkl is equal to f Cl + FC_S where h + k + l = 2n and if it is f Cl - fC_S where h + k + l = 2n + 1 see what you have to appreciate in this particular example is it is though it is BCC crystal it is the since it is chromium and BCC are two different atoms it should be considered as 2 BCC crystals are inter penetrating with each other.

It is a kind of an ordered system and you have we should also appreciate that since these two items are varied I mean different chlorine and CCM there scattering factor will be will be very different in do as an individual atom so you will see instead of in some reflections instead of a some of the peak intensities you will see the difference in that scattering power that is why you see in some terms it is + and some term it is minus here and the corresponding effect you will see in the a bigger circle here that means higher intensity that is some of intensity and then you have some of this it is the different peak this is a different peak this is a some peak.

That is what it is written the peaks for which hk h + k + l is even or some peaks that means when h + k + l is equal to 2n means a some peaks and are bigger than these those with h + k +l is odd something like the red spot here which are all different peak it is not the some peak it is called a different peak here and you get this again a reciprocal lattice cell and you will be able to appreciate this when you look at the electron diffraction pattern much more clearly you will see this kind of an evidence actual practical evidence for the difference in the intensities.

And this structure factor calculation nicely shows that the difference in the intensity is because of the factors like this.

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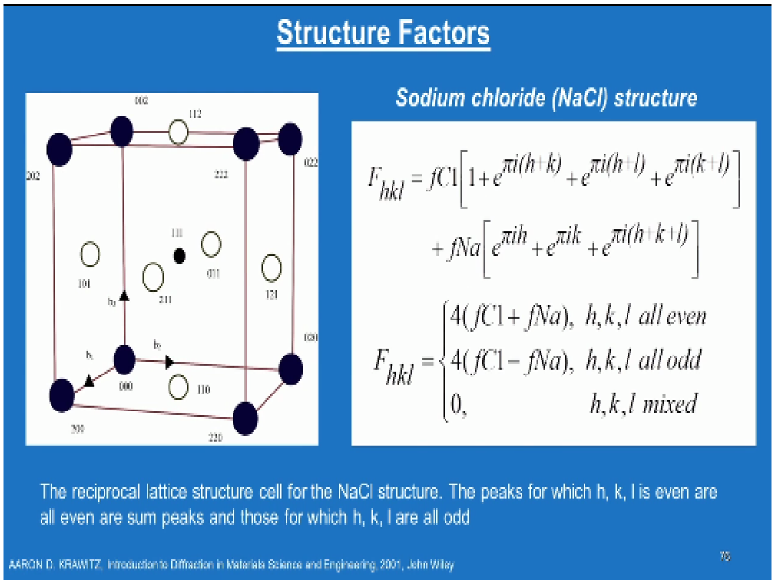

Structure Factors

Sodium chloride (NaCl) structure

$$F_{hkl} = fCl\left[1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}\right] + fNa\left[e^{\pi ih} + e^{\pi ik} + e^{\pi i(h+k+l)}\right]$$

$$F_{hkl} = \begin{cases} 4(fCl + fNa), & h,k,l \text{ all even} \\ 4(fCl - fNa), & h,k,l \text{ all odd} \\ 0, & h,k,l \text{ mixed} \end{cases}$$

The reciprocal lattice structure cell for the NaCl structure. The peaks for which h, k, l is even are all even are sum peaks and those for which h, k, l are all odd

AARON D. KRAWITZ, Introduction to Diffraction in Materials Science and Engineering, 2001, John Wiley

Now you will go on to another important a crystal system or a sodium chloride structure and this is similar to cesium chloride you have two interpenetrating FCC crystal units and you can see that the two positions are mentioned here one and I mean you can this is the final expression what we have written and you can see that F_{hkl} is equal to 4 times fCl + fNa where hkl are all even that is a some peak you will see and there is a difference peak when hkl are all odd.

And if they are mixed there is the structure factor is zero, so you can see this you can look at this selection rule and then corresponding the reciprocal lattice structure you can see that all some peak will have a higher intensity that is larger circle dark circle and then there is a different speak like 111 you will have a lesser intensity and then you have zero intensity in hkl are all mixed like this, so it is just to give you an idea how the structure factor nicely gives you the idea of the intensity summing up or it is becoming 0 or it becoming at the difference in the scattering power of the atoms.

So these illustrations clearly shows they simply demonstrate the significance of the structure factor in appreciating the x-ray diffraction intensity, so having said that we are we are only interested in appreciating the our understanding the intensity from the single crystal or it could be a polycrystalline or it be in amorphous material but we have to now look at the intensity expressions what are all the term it contains, so before we really get into that we have to appreciate what are all the factors which influence the intensity, that we have to look at it.

So before I get into that discussion let me tell you the we have when you when you look at the x-ray diffraction spectrum in every peak there are two things you have I max and you have the breadth of the peak are integrated intensity there are two these three things are very important I max is always not important but it is the integrated intensity which is important which is the area under the whole peak and this is influenced by so many factors and this we have to understand done by one.

And then how this the broadening of this intensity x-ray intensity peak is related to what we are looking at in the material that is also and another important factor we will look at one by one so I will go back to the black board again.

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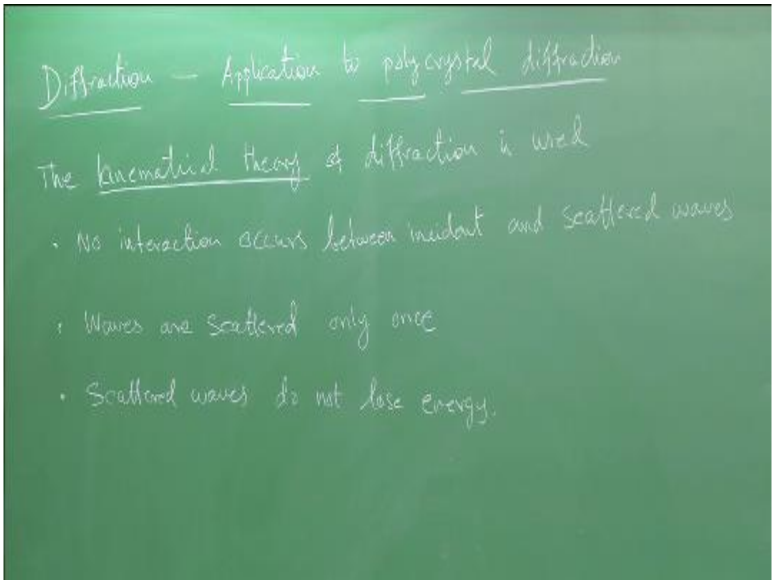

Diffraction — Application to polycrystal diffraction

The kinematical theory of diffraction is used

- No interaction occurs between incident and scattered waves
- Waves are scattered only once
- Scattered waves do not lose energy.

So before we talk about the intensity of the x-ray peak we should know what is the theory behind it in when it and it being calculations are carried out and, so you see that the kinematical theory is used for calculating the intensity of x-ray and it has got some assumption which is very important I will write down 11.3 import important assumptions you so the kinetic theory of diffraction assumes these three points that is no interaction occurs between incident and the scattered waves secondly waves are scattered only once and thirdly scattered waves do not lose energy.

So based on these assumptions the intensity of the x-ray is being calculated and then now I will just list out some of the factors which will influence the x-ray intensity.

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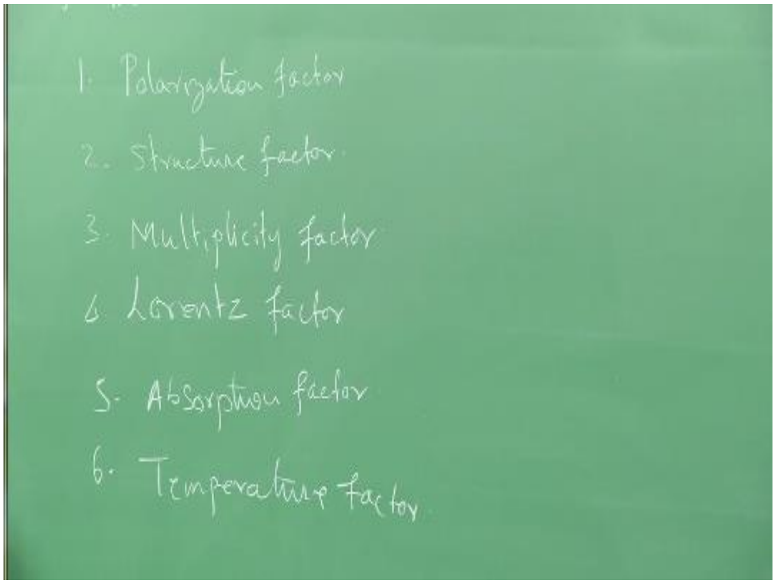

1. Polarization factor
2. Structure factor
3. Multiplicity factor
4 Lorentz factor
5. Absorption factor
6. Temperature factor

There are six factors so there are six factors that will affect the relative intensity of the diffraction lines in a polycrystalline material one is a polarization factor which we have already seen it you know you have some idea about what is polarization factor and then structure factor which we have now seen so at least these two are familiar the third one is a multiplicity factor and fourth one is Lorentz factor fifth one is absorption factor and sixth one is temperature factor.

So all these factors have to be taken into account when you write a complete intensity expression for a diffracted beam and before we get into all this you have to remember that of course this intensity also what you obtain this depending upon the method by which you perform this experiments there are primarily three methods that also I will write before we get into the intensity discussion.

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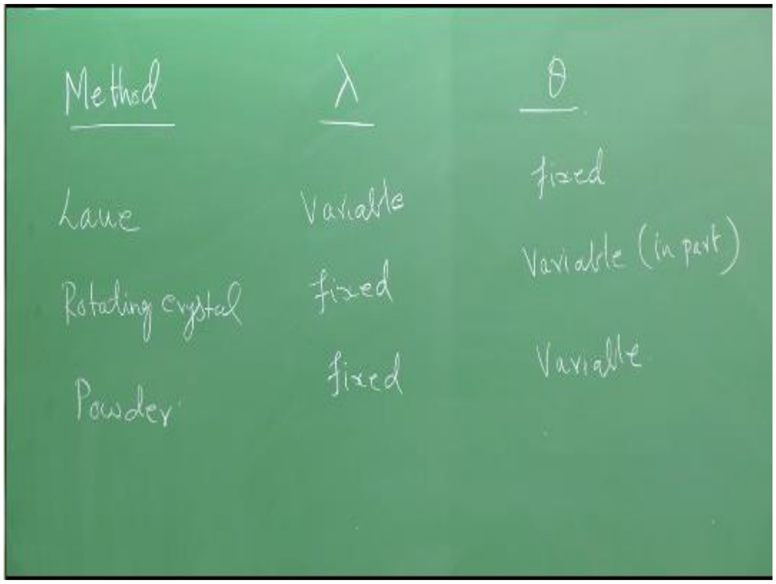

Method	λ	θ
Laue	Variable	fixed
Rotating crystal	fixed	Variable (in part)
Powder	fixed	Variable

So there are three methods one is lava method another is a rotating crystal method and third is a powder method I will not get into the theory of all these things I will take you to the lab laboratory and then actually show what are the typical methods we follow in the x-ray diffraction laboratory when we actually perform the experiment just for the sake of completion you should know the basic method of conducting this diffraction experiments when in a law a condition or a lover a method where the λ is variable and your θ is fixed in a rotating crystal method λ is fixed and your θ is variable partly and in a powder method you have a fixed λ and then variable θ these are just about the methods by which you measure the x-ray diffraction intensity for a polycrystalline material.

So we will look at the importance of the variable λ and fixed θ are fixed λ and variable θ when we do the laboratory demonstration so now we come back to the intensity of these x-rays you have to have some idea about what all these factors mean we will not get into the very detailed of the calculation of this or derivation of this which is out of the scope of this course but you should have some idea what is this factor because all these factors are going to come in the intense final intensity equation and then we will briefly go through what is this multiplicity factor and Lorentz factor and absorption factor in temperature factor so on in the next class thank you.

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