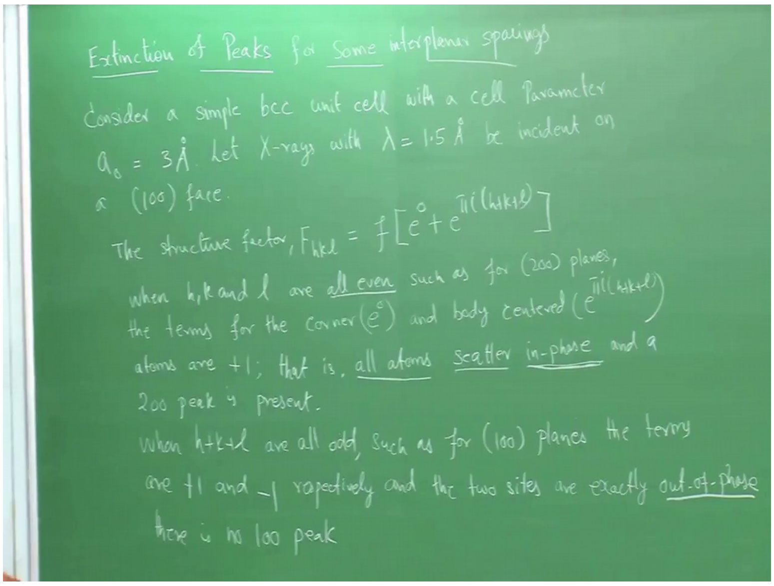
X-Ray Crystallography
Prof. R. K. Ray
MN Dastur School of Materials Science and Engineering
Indian Institute of Engineering Science and Technology, Shibpur
Department of Metallurgical and Materials Engineering
Indian Institute of Technology, Madras

Lecture - 18
Tutorial 04

(Refer Slide Time: 00:17)



Extinction of Peaks for Some interplanar spacings

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 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.

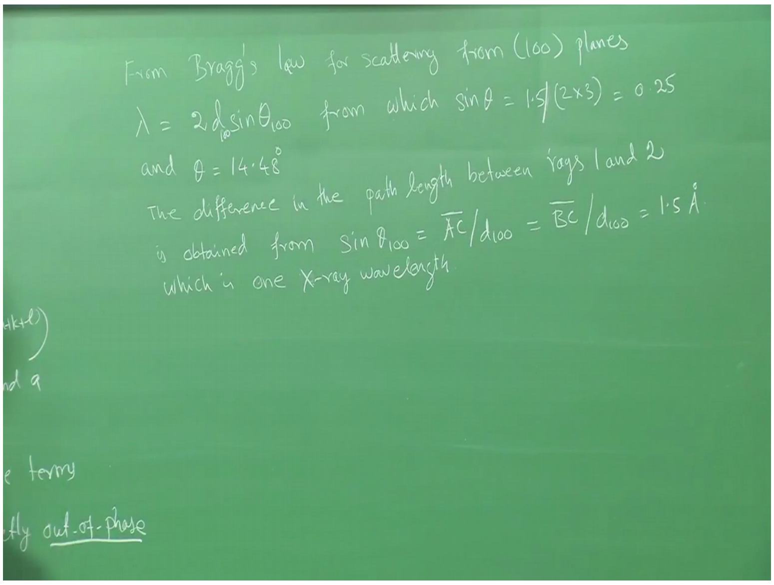
When h+k+l are all odd, such as for (100) planes the terms are +1 and −1 respectively and the two sites are exactly out-of-phase there is no 100 peak

Now we will look at the extinction of a peaks for some inter planar spacings; in this case we will take BCC unit cell I consider a simple BCC unit cell with a cell parameter a naught equal to 3 angstrom let X-rays with wavelength lambda which is equal to 1.5 angstrom be incident on the 1 0 0 phase. Now, we will calculate the structure factor. So, this is the structure factor equation because of the 2 atoms were unit cell. So, when h k l are all even fetches for 2 0 0 planes.

For example, the terms for the corner atoms that is e power 0 and the body centred atom e power pi i into h plus k plus l atoms are plus one; that means, what does that mean; that means, all atoms scatter in phase and 2 0 0 peak is present. So, according to this rule all atoms scatters in phase. So, these things you have remember and 2 0 0 peak is also present.

However, when h h plus k plus l are all on such as 1 0 0 plane the terms are plus 1 and minus 1 respectively and the 2 sides exactly out of phase when there is no 1 0 0. 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 kinds of planes naught.

(Refer Slide Time: 06:34)



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

k+l)

nd a

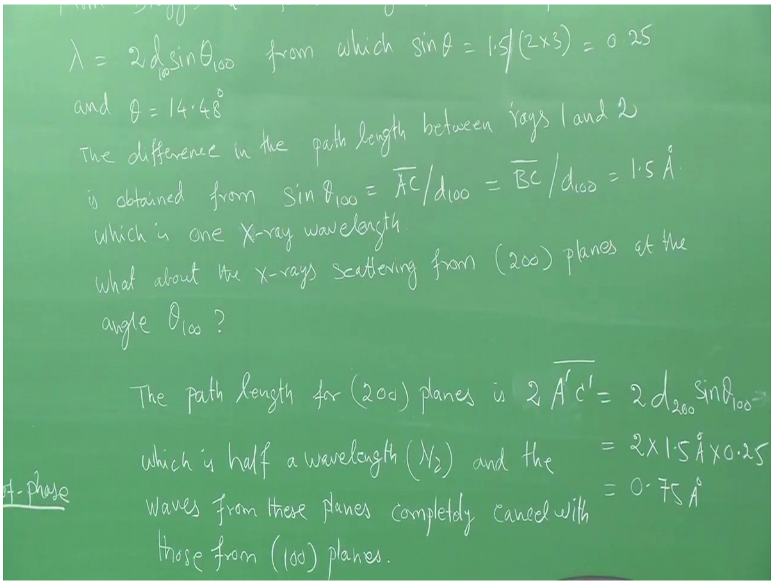
e terms

tly out-of-phase

These kind of plane because of this extinction rules now we can prove this concept geometrically we first solve Bragg's law for scattering from Bragg's law we write for scattering 1 1 planes lambda is equal to 2 d 1 0 0 .

Let us understand what we have done. So, far from the Bragg law for scattering from 1 0 0 planes you can simply write lambda is equal to 2 d 1 0 0 plane sin theta 1 0 0 from which we can find out the sin theta value sin theta is equal to 1.5 divided by 2 into 3 which is equal to 0.25 correspond to the theta 14.48; the difference in the path length between rays 1 and 2 the of the rays shown in the side you can see that we can obtain it from sin theta 1 0 0 equal to a c divided by d 1 0 0 which is equal to BC divided by d 1 0 0 which is equal to 1.5 angstrom which is one X-ray wavelength. So, that is what we have stated with.

(Refer Slide Time: 10:51)



$\lambda = 2 d_{100} \sin\theta_{100}$ 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 $2\overline{A'C'} = 2 d_{200} \sin\theta_{100}$

$= 2 \times 1.5\,Å \times 0.25$

$= 0.75\,Å$

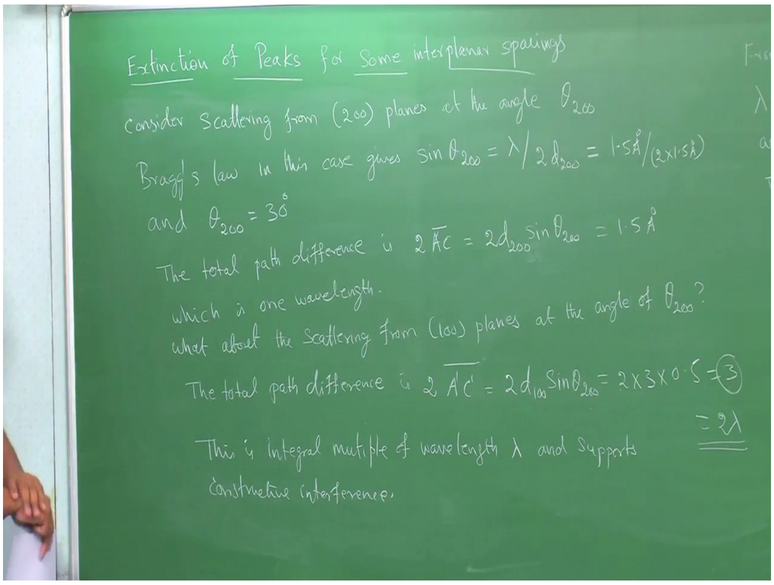
which is half a wavelength ($\lambda/2$) and the waves from these planes completely cancel with those from (100) planes.

-phase

So, it is 1 X-ray wavelength now the question is what is what about the X-rays scattering from 2 0 0 planes at the angle theta 1 0 0. So, we can find out in similar way the path length let me rewrite. So, the path length for 2 0 0 planes is 2 times A dash C dash which is equal to 2 d sin theta 1 0 0, we can substitute this you will get 0.75 as path length which is half of the;

So, what the consequence if you have the path length from 2 0 0 planes is exactly half the wavelength. As we have discussed previously it will completely cancel out the intensity we can write that which will. So, when you have the path length for 2 0 0 planes is as half a wavelength then the wave from these planes completely cancel with those from 1 0 0 planes that is why you do not see the peaks 1 0 0 3 0 0.

(Refer Slide Time: 15:55)



Extinction of Peaks for Some interplanar spacings

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

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

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

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

which is one wavelength.

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

The total path difference is $2\overline{A'C'} = 2d_{100}\sin\theta_{200} = 2 \times 3 \times 0.5 = \boxed{3}$

$= 2\lambda$

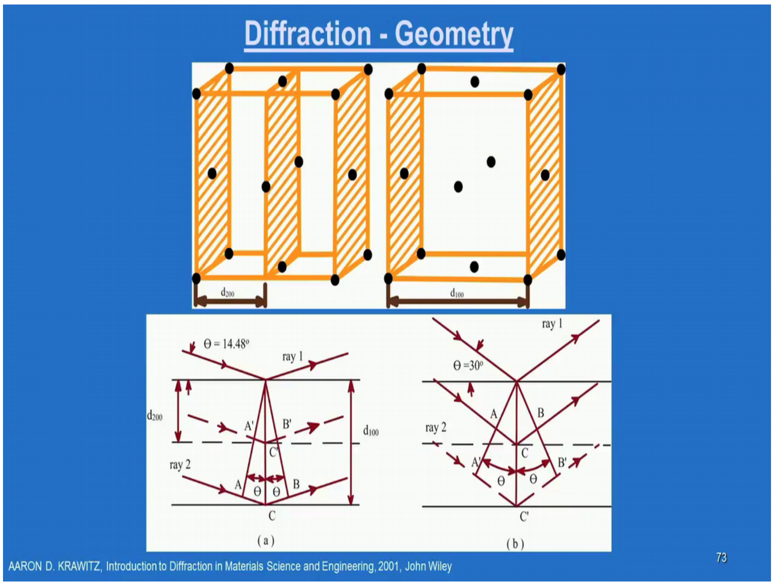
This is integral multiple of wavelength λ and Supports constructive interference.

And. So, on in that reciprocal lattice now let us consider the scattering from. So, let us consider these scattering from 2 0 0 planes at the angle theta 2 0 0 if you look at the slide the figure b shows this schematic excuse me. And then we will proceed with the calculations and the Bragg law for this case gives sin theta 2 0 0 is equal to lambda by 2 d 2 0 0 which is nothing but 1.5 angstrom divided by 2 times 1.5 angstrom which is worked out to theta 2 0 0 is 30 degree.

Now, at this angle the total path difference the total path difference is 2 times a c which is 2 d 0 0 sin theta 2 0 0 which is nothing but 1.5 angstrom which is nothing but one wavelength. Now similar question what we have asked there what about scattering from. So, similar question here what about the scattering from 1 0 0 planes at the angle of theta 2 0 0. Now then we can work it out this also the total path difference. So, the total path difference in the case of scattering from 1 0 0 plane at the angle of theta 2 0 0 is 2 times a prime c prime which is equal to 2 d 1 0 0 sin theta 2 0 0 which is equal to 2 into 3 into point five which is nothing but 3 3 is 2 lambda this value is nothing but 2 lambda this is which is nothing but an integral multiple of a wavelength length lambda and supports the constructive inter prints process.

So, from this example we have seen how this 2 0 0 type of planes exist and what is the meaning of extinction of certain peaks in for some inter planar spacing in crystal in cubic crystal like a BCC. So, these 2 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 come back to this slides if you look at this slide this is structure factor calculation for a phase centred cubic structure.

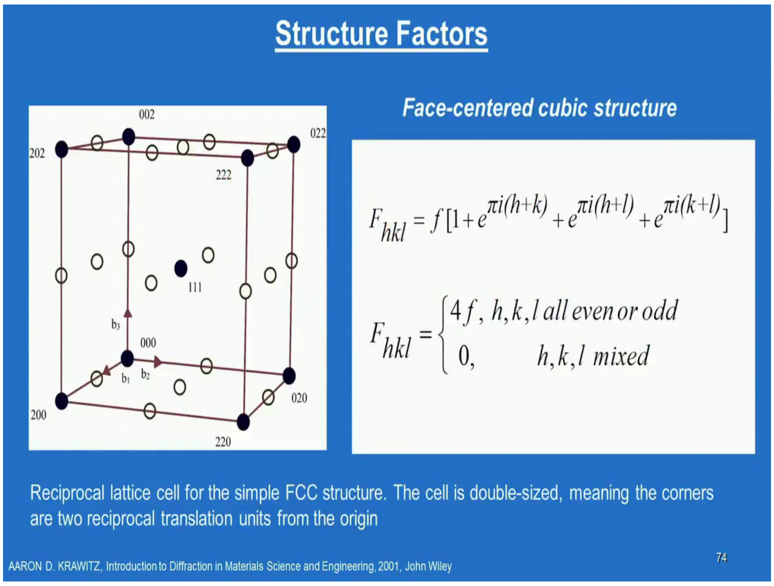
(Refer Slide Time: 23:03)



Diffraction - Geometry

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

(Refer Slide Time: 23:08)



Structure Factors

Face-centered cubic structure

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

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

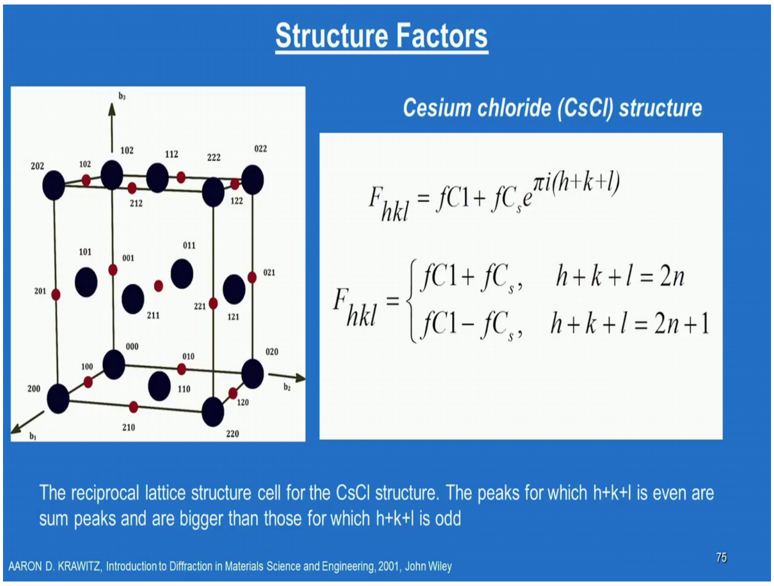
Reciprocal lattice cell for the simple FCC structure. The cell is double-sized, meaning the corners are two reciprocal translation units from the origin

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

And if you write the expression you have atoms per unit cell. So, you get the 4 terms here. So, 1 plus e pi i h plus k plus e pi i e to the power pi i h plus l plus e to the power pi i into k plus l. So, the rule is f h k l is equal to 4 f where h k l all even or add and the intensity will become our structure factor will become 0 when h k l are mixed.

So, now you see that this is again a reciprocal lattice cell. So, do not confuse this with your real cell this is reciprocal unit cell. 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 h k l all even or all odd will have the allowed reflections. So, other positions are forbidden. So, what you can now appreciate is the reciprocal unit cell or an FCC lattice actually a BCC lattice it does the same thing what we have see before it is the other way around for an real BCC lattice the reciprocal lattice is an FCC unit cell. So, that is clearly appreciated here.

(Refer Slide Time: 24:59)



Structure Factors

Cesium chloride (CsCl) structure

$$F_{hkl} = fC1 + fC_s e^{\pi i(h+k+l)}$$

$$F_{hkl} = \begin{cases} fC1 + fC_s, & h+k+l = 2n \\ fC1 - fC_s, & h+k+l = 2n+1 \end{cases}$$

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

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

75

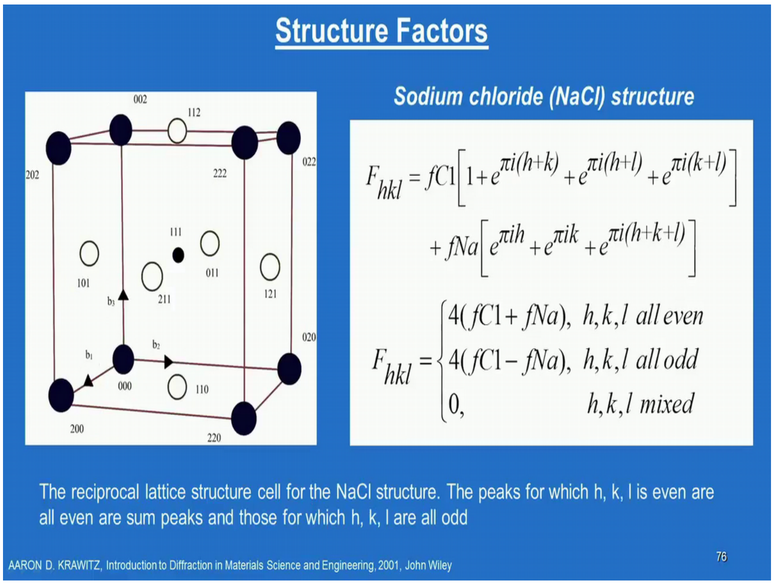
Now we will see some interesting examples a caesium chloride structure where you have a caesium chloride type of structure you can see that it is kind of body centred unit cell has got 2 atoms that is chlorine and caesium atoms per unit cell which is one corner another is in the body centred position, but you can write the expression in terms of the structure factor equation like this and the selection rule is you see f h k l is equal to f C l plus f C s where h plus k plus l is equal to 2 n and if it is f C l minus f C s where h plus k plus l is equal to 2 n plus 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 caesium are 2 different atoms it is to be considered as 2 BCC crystals are interpenetrating with each other it is a an ordered system. And you should also appreciate that since these 2 atoms are very I mean different chlorine and caesium their scattering factor will be will be very different individual as an individual atom.

So, you will see instead of some some reflections instead of a sum of the peak intensities you will see the difference in that scattering power that is why you see in some terms it is plus and some term it is minus here and the corresponding effect you will see in the bigger circle here. That means, higher intensity that is sum of intensity, and then you will have sum of these it is the difference peak this a different peak this is a sum peak that is what it is written the peaks for which h k h plus k plus l is even or sum peaks. That means, when h plus k plus l is equal to 2 n means a sum peaks and are bigger than the those with h plus k plus l is odd something like the red spot here which are all difference peak it is not the sum peak it is called a difference peak here.

And this is 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 these 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 intensities, because of the factors like this.

(Refer Slide Time: 28:12)



Structure Factors

Sodium chloride (NaCl) structure

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

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

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

76

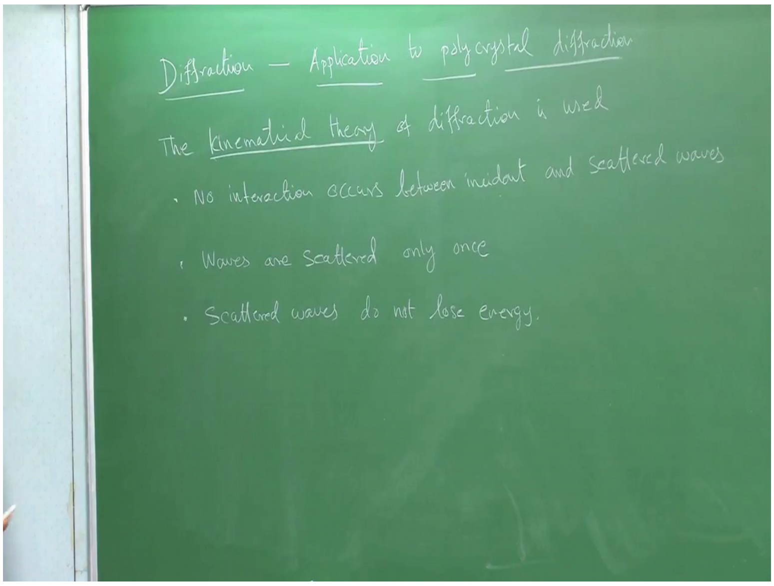
Now, we will move on to another important actors to system called a sodium chloride structure and this is similar to caesium chloride you have a 2 interpenetrating FCC crystal units. And you can see that the 2 positions are mentioned here one in I mean you can this is the final expression what we have written and you can see that f h k l is equal to 4 times f C l plus f n a where h k l are all even that is a sum peak you will see and there is a difference peak when h k l are all odd and if they are mixed there is the structure factor is 0.

So, you can see this you can look at this selection role and then corresponding the reciprocal lattice structure you can see that all some peak will have higher intensity that is larger circle dark circle and then there is a difference peak like 1 1 1 you will have a lesser intensity. And then you have a 0 intensity in h k l are all mixed like this. So, it is just to give 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 show they simply demonstrate the significance of the structure factor in appreciating the X-ray diffraction intensity. So, having said that we are only interested in appreciating the or understanding the intensity from the a single crystal or it could be a poly crystal or it could be an 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 2 things you have I max and you have the breath of the peak or the integrated intensity there are 2 these 3 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 one-by-one and then how the broadening of this intensity X-ray intensity peak is related to what we are looking at in the material. That is also an another important factor we will look at one-by-one. So, I will go back to the black board again.

(Refer Slide Time: 32:02)



Diffraction — Application to polycrystal diffraction

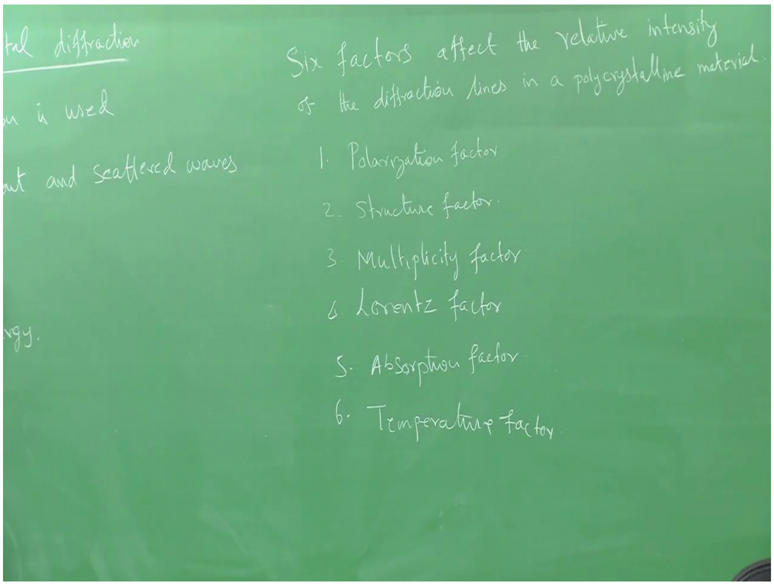
The kinematical theory of diffraction is used

- 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 when it when 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. So, I will write down 1 1 3 important assumptions.

So, the kinematic theory of diffraction assumes these 3 points that is no interaction occurs between incident and the scattered waves. Secondly, waves are scattered only once. And thirdly, scattered waves loose energy. So, based on these assumptions the intensity of the X-ray is been calculated and then now I will just list out some of the factors which will influence the X-ray intensity.

(Refer Slide Time: 35:39)



tal diffraction

n is used

nt and scattered waves

rgy.

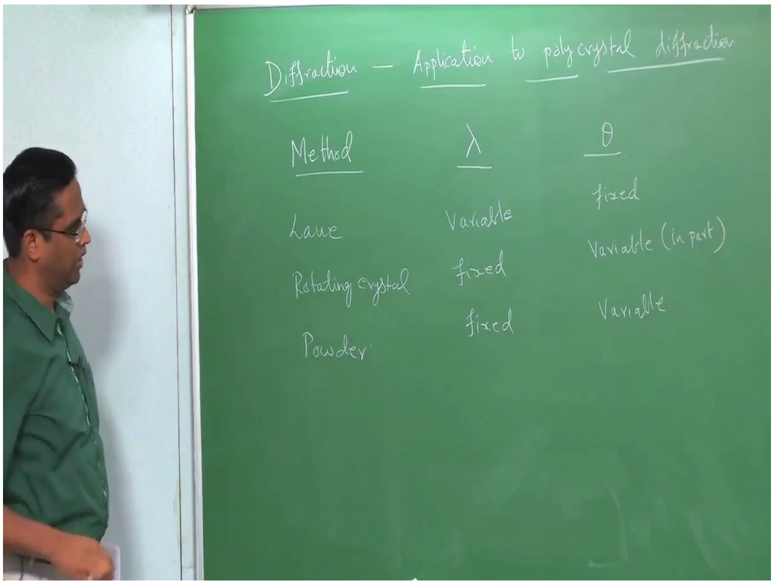
Six factors affect the relative intensity of the diffraction lines in a polycrystalline material.

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

There are 6 factors. So, there are 6 factors that will affect the relative intensity of the diffraction lines in a poly crystal 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 2 are familiar the third one is 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 in to all these you have to remember that of course, this intensity also what you obtained is depending upon the method by which you perform these experiments there are primarily 3 methods that also I will write before we get in to the intensity discussion.

(Refer Slide Time: 39:00)



Diffraction — Application to polycrystal diffraction

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

So, there are 3 methods one is lave method another is 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 laboratory and then actually show what are all the typical methods we follow in the X-ray diffraction laboratory, when we actually perform the experiment just for the a sake of completion. You should know the basic method of a conducting this diffraction experiments when in a lave condition or lave method where the lambda is variable.

And your theta is fixed in a rotating crystal method lambda is fixed and your theta is variable partly and is a powder method you have a fixed lambda. And then variable theta these are all just about the methods by which you measure the X-ray diffraction intensity for polycrystalline material. So, we will look at the importance of the variable lambda and fixed theta or fixed lambda and variable theta when we do the laboratory demonstration.

So, now we will 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 scope of this course, but you should have some idea what is this factor because all these factors are going to come in the final intensity equation. And then we will briefly go through what is this multiple multiplicity factor and Lorentz factor and absorption factor and temperature factor in the next class.

Thank you.