X-Ray Crystallography

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Lecture - 16
Intensity of Diffracted Beams-continued

I have already discussed the polarization factor, atomic scattering factor, and crystal structure factor which affect the intensities of the diffracted lines in the pattern taken by Debye Scherrer camera. Now I will talk about another important factor known as the Lorentz factor.

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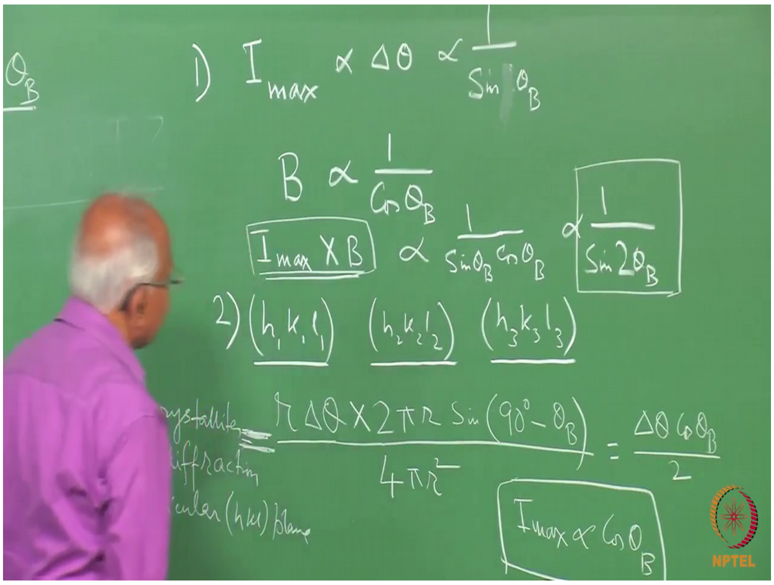

The Lorentz factor is actually a combination of 3 geometrical factors and these factors are based on the following facts. Number one intensity of a diffracted beam is also appreciable at angles deviating slightly from the exact Bragg angle. So, this is quite important.

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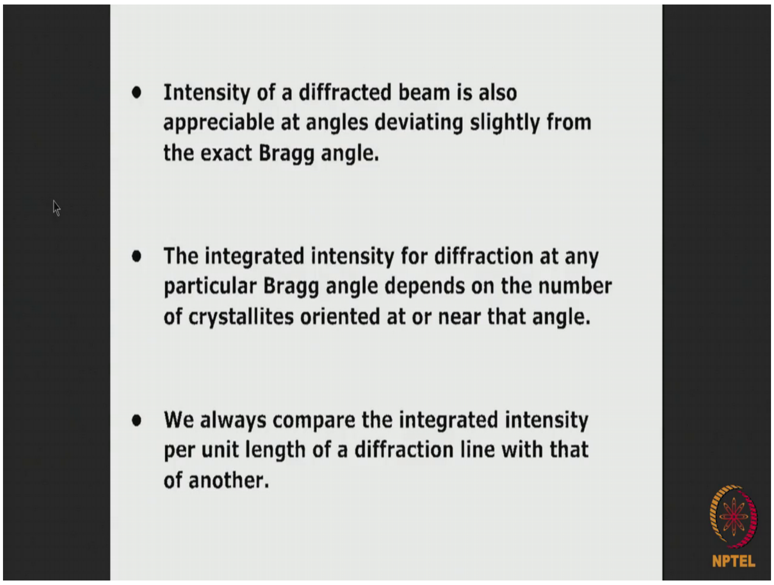

- Intensity of a diffracted beam is also appreciable at angles deviating slightly from the exact Bragg angle.
- The integrated intensity for diffraction at any particular Bragg angle depends on the number of crystallites oriented at or near that angle.
- We always compare the integrated intensity per unit length of a diffraction line with that of another.

The second fact is the integrated intensity for diffraction at any particular Bragg angle will depend on the number of crystallites oriented at or near that angle, and the third fact is we always compare the integrated intensity per unit length of a diffraction line with that of another. Based on these facts 3 geometrical factors can be considered which will constitute the Lorentz factor.

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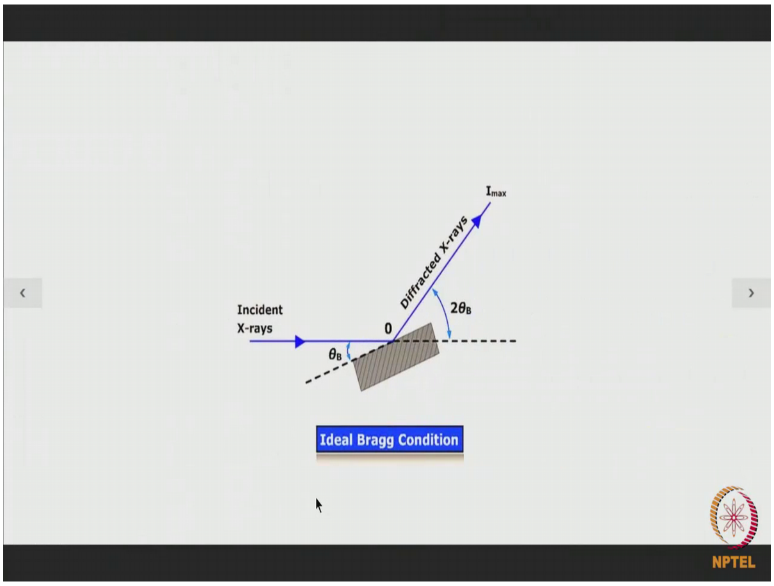

Ideal Bragg Condition

Now, on the ideal Bragg condition when the X rays are incident at the correct Bragg angle with respect to atomic planes within a sample we expect to get a diffracted beam of X rays making an angle 2 theta B with respect to the incident X radiation; however, what we find in practice is that.

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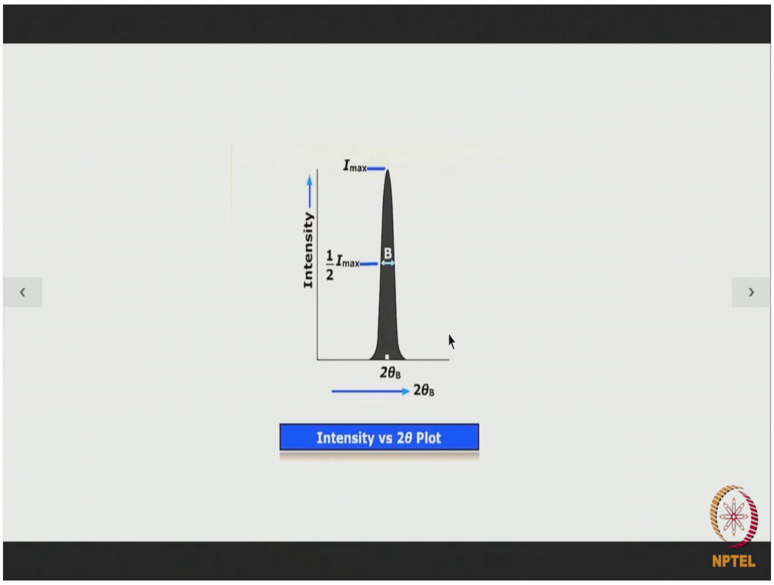

Intensity vs 2θ Plot

If we plot intensity versus 2 theta B at the correct Bragg position we get not only a high enough intensity, but there is some intensity available even for angles other than the Bragg angle on both sides. So, this indicates that there is some diffracted intensity even when we are slightly deviating from the exact Bragg condition. As a result of which the intensity versus 2 theta B plot does not show a straight line only at the correct 2 theta B, but the line profile shows a shape of this type.

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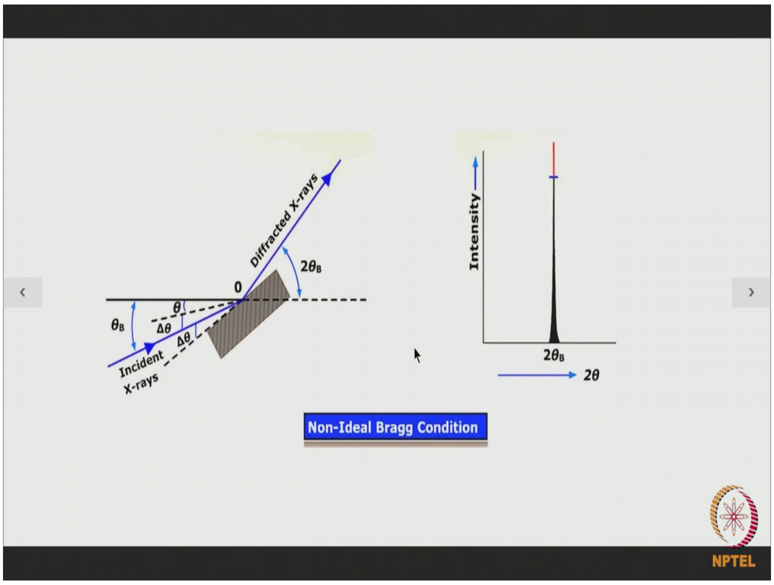

Non-Ideal Bragg Condition

Now let us suppose that we are having a non ideal Bragg condition say for example, if this is the incident angle from the X radiation, and if this is diffracted rays that this is the 2 theta B we can have this situation where the incident angle is not exactly theta B, but slightly less or slightly higher than theta B. So, these 2 conditions are given by this line and this line. So, the incident radiation if it is falling on the crystal surface and angles slightly lower or slightly higher than theta B the Bragg angle, what situation will arise we now examine that.

Now here the delta theta the deviation from the exact Bragg angle as we shown on a very very magnified scale you see you know for in order to understand this clearly now the situation is even when the angle of incidence is slightly lower or slightly higher than the exact Bragg angle, then also in the original direction of diffracted X rays we will have some contribution due to the incoming X rays. That means, if the height from the base to this point is due to diffraction on the ideal condition at 2 theta B position, there will be some extra intensity also due to the non ideal condition of diffraction. So, we say that the maximum intensity which we get during diffraction will be mostly composed of the diffracted intensity on the ideal Bragg condition plus a little bit extra due to diffracted intensity from non ideal condition.

If we go back to the previous figure, we say that the diffraction profile has got a shape like this. So, this is the maximum intensity now if we come down to a intensity level which is half of I max the breadth of the diffraction profile b is a very important parameter. So, if we want to find out the total intensity of diffraction from a set of atomic planes, we have to consider you know the whole intensity not only at the 2 theta B position, but also at the other positions.

You see when the exact Bragg law is satisfied we get the maximum intensity of the diffracted beam this is due to the fact there is 100 percent constructive interference of the rays scattered by the different atoms, but even when there is a 100 percent constructive interference then also we will get some intensity that intensity will be much much lower than when there is 100 percent constructive interference and that is the reason why we get a line profile of this shape and the total intensity of diffraction from this particular for this particular line you know will be proportional to the area of this line profile or in other words it will be proportional to I max multiplied by B.

As I have already told you that under non ideal Bragg condition there will be some intensity extra intensity which will also be there at the extra at the 2 theta B position. So, this much of intensity is due to the situation where exact Bragg law is satisfied, and this extra comes from the fact that even when you know the Bragg condition is fully satisfied there is a slight deviation or the incident angle from the Bragg angle, the also some intensity will appear at 2 theta B.

Now we say that this intensity at 2 theta B will depend on the value of delta theta. If you can have a large larger value of delta theta when some intensities still possible to have in 2 theta B position then you will get extra intensity in the diffracted beam. So, the intensity of the diffracted beam or rather the I max will be proportional to the value of delta theta.

So, this can be written as I max to be proportional to the value of delta theta and it can be shown at this is proportional to 1 upon sin 2 theta B, that is proportional to 1 upon I am sorry it is proportional to upon sin theta B, it is proportional to 1 upon sin theta B. So, we say that due to non ideal condition of diffraction I max it is proportional to delta theta will be proportional to 1 upon sin theta B this I am saying without any proof.

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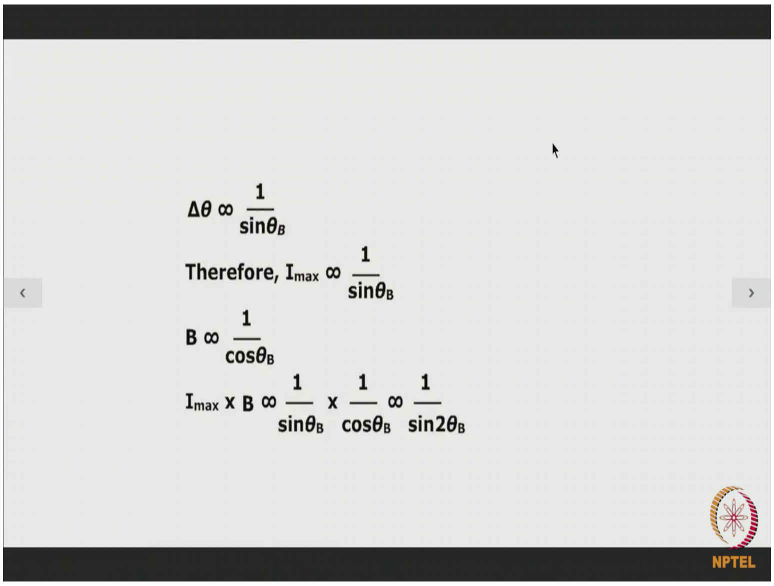

$\Delta\theta \infty \frac{1}{\sin\theta_B}$

Therefore, $I_{max} \infty \frac{1}{\sin\theta_B}$

$B \infty \frac{1}{\cos\theta_B}$

$I_{max} \times B \infty \frac{1}{\sin\theta_B} \times \frac{1}{\cos\theta_B} \infty \frac{1}{\sin 2\theta_B}$

Now if we look at the breadth of the line for line B, then also it can be shown that this is proportional to I above cosine theta B. So, you say that delta the I max is proportional to 1 by sin theta B, I have shown it without any proof. Similarly it can also be shown that b the breadth of the line profile is proportional to 1 upon cosine theta B. Now the integrated intensity which will be proportional to I max into b will be proportional to 1 upon sin theta B cosine theta B. So, this will be proportional to 1 upon sin theta B, 1 upon cosine theta B; that means will be proportional to 1 upon sin 2 theta B.

So, we realize that the integrated intensity of a diffraction line which is proportional to the maximum intensity available at 2 theta B and the breadth of the line at half maximum intensity is also proportional to 1 upon sin2 theta B.

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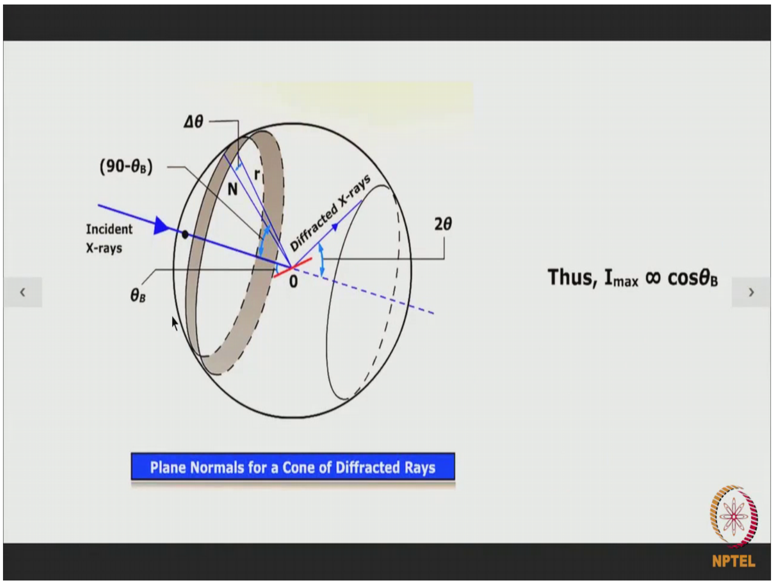

Thus, $I_{max} \propto \cos\theta_B$

Plane Normals for a Cone of Diffracted Rays

So, this is the first geometrical factor that comes into the Lorentz factor. Now let us talk about the second geometrical factor which is also part of the Lorentz factor. Say for example, if you have a sample here this shows an atomic plane which is poised for diffraction. This is the incident beam which is incident at an angle of theta B the Bragg angle and say- this is the diffracted beam of X rays this is 2 theta B.

Now we normally assume that only crystallites arrange in a powder sample there are arranged in a redundant fashion therefore, the number of crystallites which will give rise to diffraction from a particular atomic plane will be the same as the number of crystallites you know which diffract crystallites which will be diffracting from a you know particular another particular plan,e etcetera, etcetera.

That means since the arrangement since there are the total number of crystallites in a powder sample they are arranged in a random fashion therefore, it is sometimes you know it is very natural to assume that we will have a similar number of crystallites, which will give rise to all the different diffracted beams from the different planes; that means, if you have a plane h 1, k 1, l 1 if you have a set of planes h 1, k 1, l 1 then h 1 k 2, l 2 and say h 3, k 3, l 3. So, since all the crystallites in the polycrystalline sample in a Debye Scherrer camera they are randomly arranged; it will be quite natural to assume that the number of crystallites within the sample which give rise to diffraction from this plane will be the same as the number of crystallites which give rise to diffraction from this type of planes will be equal to the number of crystallites which give raise to diffraction from this type of planes, but this is not actually true as will we see right now.

Say for example, in this particular case O N is the normal to the h k l plane shown here wave is a normal to the h k l plane shown here. We know that even when non ideal Bragg condition is fulfilled there will be some diffraction; that means, we can find out that even when you know the perpendicular to the h k l plane is not O N, but slightly deviated from this say by angle delta theta then also we will have diffraction in the 2 theta B direction.

So, these 2 lines they will specify a ribbon like element within a sphere which we draw with O as the centre. So, we can say that all the crystallites that will be available to diffract from this particular h k l planes, they are plain normal’s you know that they are they will appear within these ribbon element within this ribbon element. So, the total number of crystallites which are available for diffraction from this particular atomic plane, the number will be proportional to the area of this ribbon like element.

And if we consider the total number of crystallites in the sample at O then the total number of crystallites their number will be proportional to the area of the entire sphere. So, you see that these ribbon like element the area of the ribbon like element, will vary depending on the h k l plane. So, that is the reason why even though we have you know the crystallites arranged in a very random fashion in the polycrystalline sample, the number of crystallites which will give raise to diffraction from a particular plane will very from plane to plane. So, in this particular case diffraction will occur from a number of crystallites whose number is proportional to the area given by this ribbon element.

So, what is the fraction of crystallites that we will get what is the fraction of what is the fraction of crystallites that will diffract radiation from this particular plane you see if you look at the ribbon like element here if you look at the ribbon like element, this angle is delta theta. So, if the radius of this ribbon like element is small r r delta theta will be the width of the ribbon. So, r delta theta will be the width of the ribbon and what is the length of the ribbon? Length of the ribbon will be 2 r 2 pi r sin 90 degree minus theta B.

So, you say that this is the width of the ribbon and this is the length of the. So, the total area of the ribbon is given by r delta theta multiplied by 2 pi r sin 90 degree minus theta B. So, the total number of crystallites in the polycrystalline sample which will give raise to diffraction from this particular atomic plane h k l plane will be proportional to this value.

And the total number of crystallites in the sample itself there will be the number will be proportional to the area of the entire sphere, surround at centre at the point o and we know that that area is 4 pi r square. So, this is nothing, but the fraction of crystallites.

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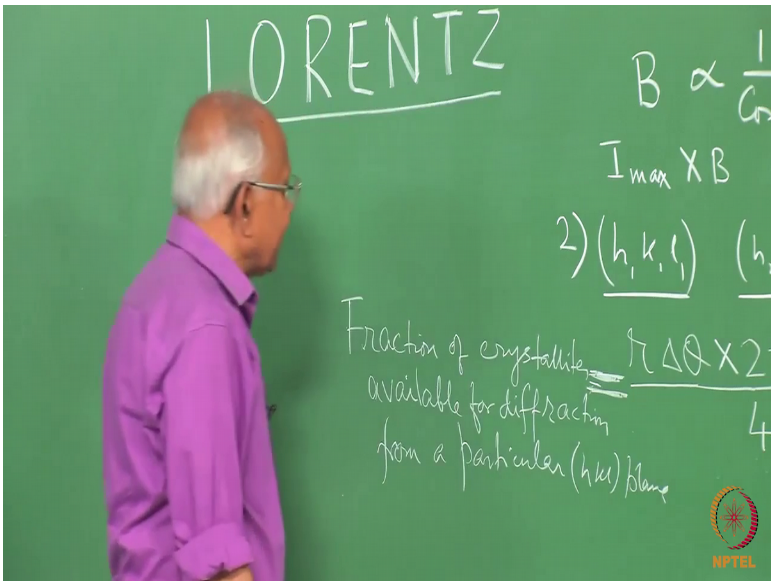

This is the fraction of crystallites available for diffraction from a particular h k l plane. So, this is a very important thing, you see normally we assume you know we have the idea that since the total number of crystallites in the polycrystalline sample in the Debye Scherrer method they are randomly arranged. So, the number of crystallites within the sample which will give raise to diffraction from h 1, k 1, l 1 plane or from h 2, k 2, l 2 plane or from h 3, k 3, l 3 plane they should be similar, but this is not true simply because of the fact that the fraction of crystallites available for diffraction by particular h k l plane it is different.

So, all other factors remaining constant only because of this fact the intensity of the diffracted beams will vary now. So, this fraction will be equal to it will be equal to delta theta cosine theta B divided by 2. So, it immediately tells us that I max the intensity diffracted in this particular direction will be proportional to cosine theta B.

So, I max will be proportional to cosine theta B. So, this is the second geometrical factor which constitute the Lorentz factor. The though first one was that the integrated intensity the I max into b is proportional to 1 by sin 2 theta B, the first factor was this the second factor is the fraction of crystallites available for diffraction from a particular h k l plane, because it is different I max will be proportional to cosine theta B now let us talk about the third geometrical factor.

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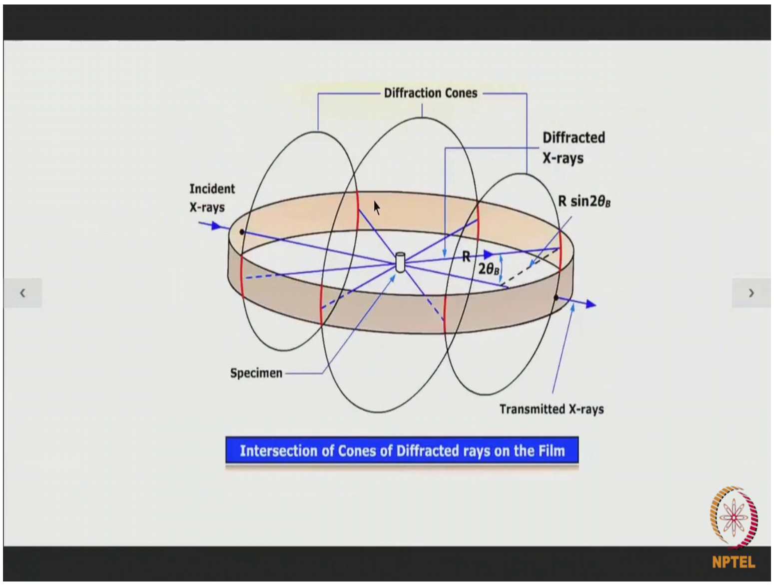

Intersection of Cones of Diffracted rays on the Film

You see when we talk about a diffraction line say for example, in the Debye Scherrer method these 3 indicate 3 diffraction cons from 3 different diffracting planes. So, these 3 show the 3 diffracting cons of radiation from 3 diffracting planes. Now the arrangement of the film is such that we do not record the entire intensity that is present over the cone we measure only a part of it in the on a part of in the film say for example, here. So, the total intensity diffracted should be calculated over the entire circular area of the Debye Scherrer ring.

Similarly for this case also the entire you know the total integrated intensity should be considered from this entire Debye Scherrer ring, but we are not doing that actually we measure the intensity on unit length from each cone. So, because of the arrangement and the shape of the recording film we record only a little bit say unit length of the total length of a diffraction cone in every case. So, you see that because of that what will happen the intensity measured from the lines on a Debye Scherrer pattern those will be underestimating the total diffraction intensity in this case, and will be overestimating the total diffraction intensity in this case.

And because of that we have to have some factor which must be multiplied which must be used in order to rationalize the intensities from the different h diffractions form the different h k l planes now if you look at the size of the cone here.

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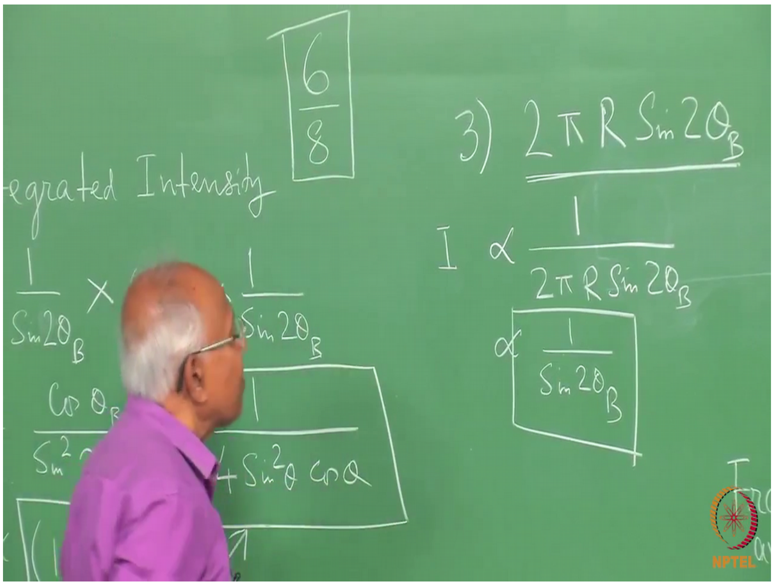

So, this angle is 2 theta B. So, naturally and if this is the r is the radius of the camera, then we can write down that the length of the cone the base of the cone is 2 pi r into sin 2 theta B. So, the length of the base of the cone in a particular case is equal to say this is r this angle is 2 theta B this length will be 2 pi r sin 2 theta B, where r is the radius of the camera. So, we do not measure the intensity over the entire length of the base of the cone, we measure the intensity from say unit length from this cone.

So in fact, our integrated intensity our integrated intensity is proportional to 1 upon 2 pi r sin 2 theta B; that means, I is proportional to 1 upon sin 2 theta B. So, this is another important relationship that we get. So, from the first condition we found that I max b the integrated intensity of a diffraction line is proportional to 1 upon sin 2 theta B, then in the second case we find that I max is proportional to 2 sin theta B and again over here actually this is the this is the total integrated intensity is proportional 2 I 1 upon sin 2 theta B.

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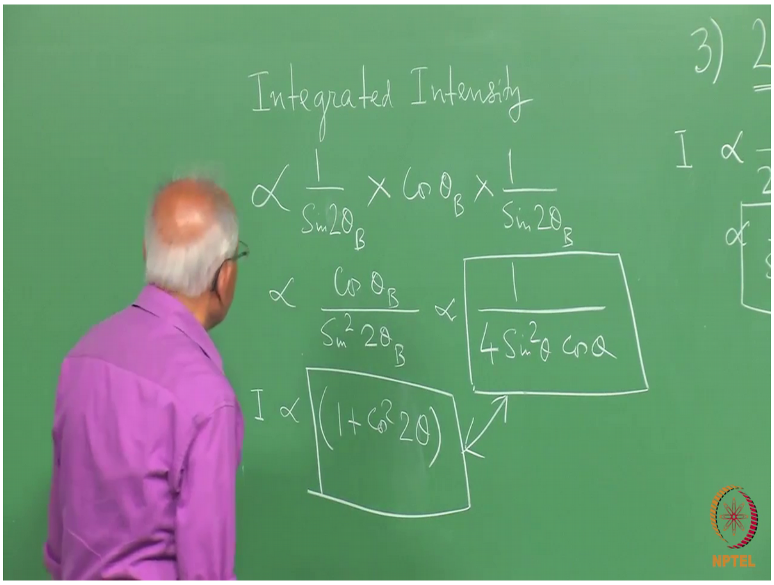

So, if we look at the integrated intensity you know if you combine these 2 factors. So, if we combine integrated intensity if we combine these 3 geometrical factors then we find the integrated intensity will be proportional to 1 by sin 2 sin 2 theta B multiplied by the second one cosine theta B multiplied by the third one1 by sin 2 theta B. So, this will be proportional to cosine theta B by sine square 2 theta B, or this will be proportional to if we break it down further it will be proportional to 1 upon 4 sin square theta cosine theta it will be 1 upon 4 sin square theta cosine theta.

So, we say that because of these 3 geometrical factors, the integrated intensity will be proportional to for any line will be proportional to this value 1 by 4 sin square theta cosine theta. Now if we remember while you determine the polarization factor in the polarization factor the integrated intensity were found to be proportional to 1 plus cosine square theta. So, this is what I am sorry cosine square 2 theta in the in case of the polarization factor, we found out that the integrated intensity is proportional to 1 plus cosine square 2 theta.

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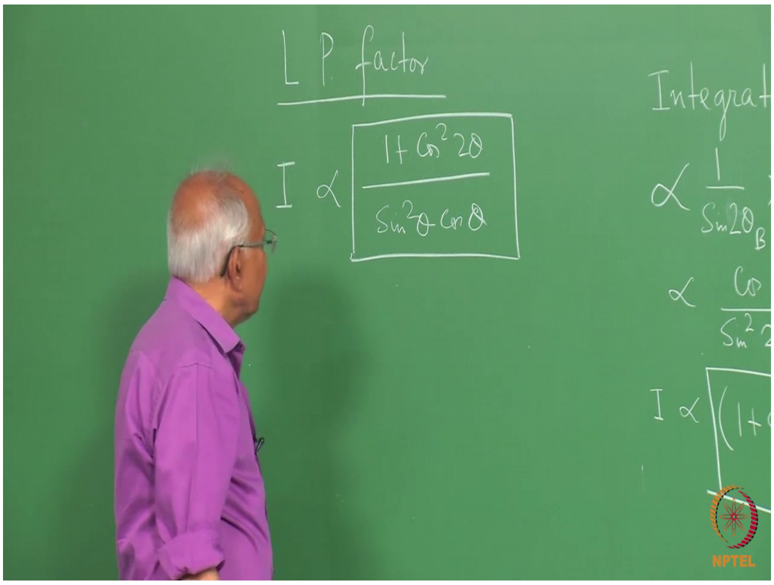

So, now we can combine this with this and we can find out we can say that if we talk about the Lorentz factor as well as the polarization factor.

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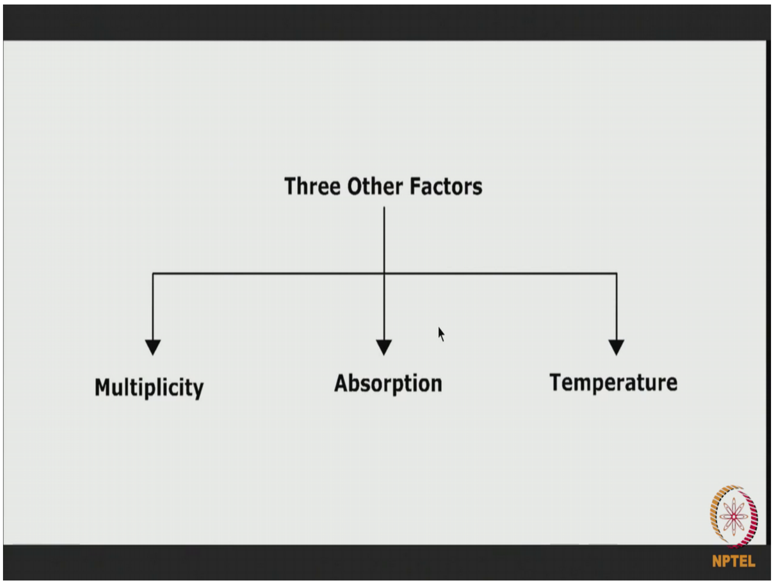

Three Other Factors

Multiplicity

Absorption

Temperature

Then the Lorentz polarization factor it says that integrated intensity of a diffraction line will be proportional to one plus cosine square 2 theta divided by sin square theta cosine theta you know this 4 we have taken out is a constant. So, we say that the due to the effects of both the polarization factor and the Lorentz factor the integrated intensity will be proportional to this quantity one plus cosine square 2 theta divided by sine square theta cosine theta. Now 3 other factor are remaining to be discussed and those are the multiplicity factor the absorption factor and the temperature factor.

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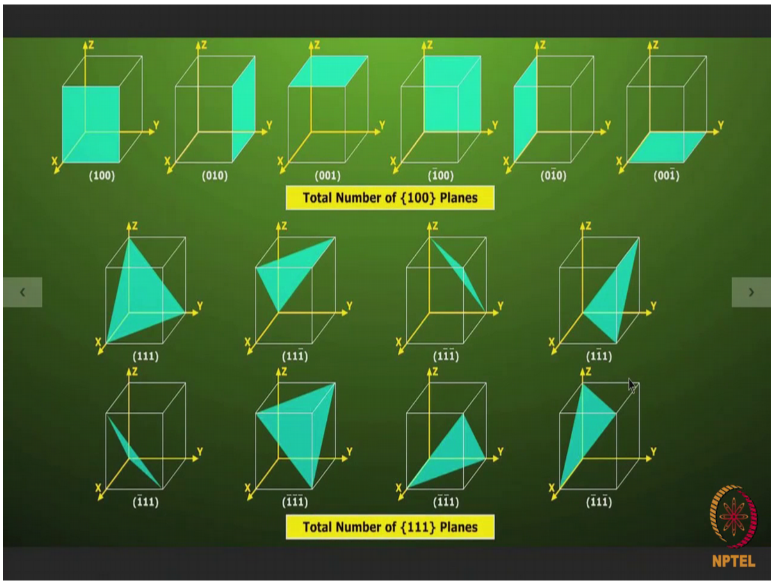

Total Number of {100} Planes

Total Number of {111} Planes

Now, what is the multiplicity factor? You see every other factor remaining constant if we find that in a particular system of planes say 1 0 0 how many 1 0 0 planes are there are 6 different types of 1 1 1 0 0 planes similarly if we talk about the 1 1 1 planes there are 1 2 3 4 5 6 7 8 with different indices.

So, there are 8 planes are there. So, every other factor remaining constant when we find out diffraction from the 1 0 0 planes and diffraction from the 1 1 1 planes, then we will see that the ratio of the diffracted intensity should be 6 by 8 only because of the fact that the number of planes in a particular system of planes is not equal. So, all other factors remaining constant the since the 1 0 0 type planes there are 6 of them and 1 1 1 planes there are 8 of them. So, integrated intensity from the 1 0 0 plane divided by the integrated intensity from the 1 1 1 type of planes will be simply 6 by 8.

So, this number 6 for 1 0 0 plane, 8 for 111 planes these are known as the this is known as the multiplicity factor. So, multiplicity factor for 1 0 0 0 planes is simply 6, and multiplicity factor from for 1 1 1 planes is 8 in a similar manner we can find out the multiplicity factor of the other type of planes and naturally in the integrated intensity has to be multiplied by the multiplicity factor in every case, then comes what is known as the absorption factor.

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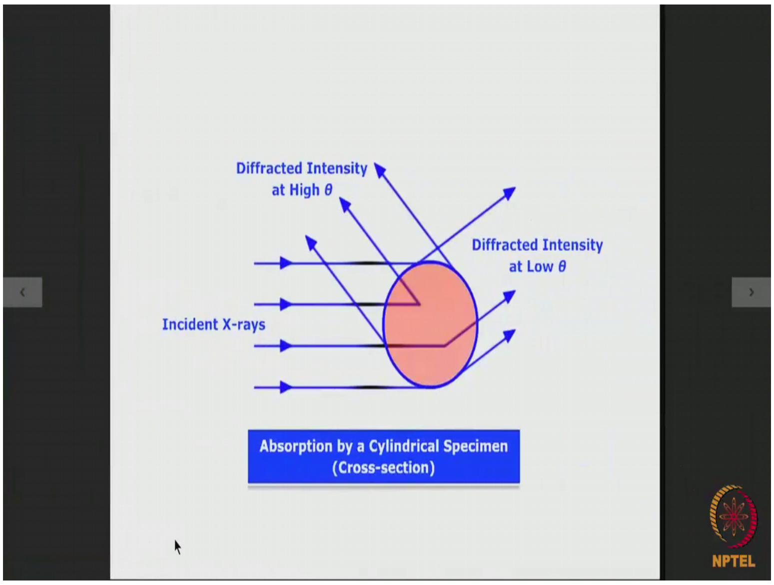

Absorption by a Cylindrical Specimen
(Cross-section)

Now, if we have a cylindrical specimen like this if we have a beam of X rays incident in this fashion in this direction, and if we consider diffracted intensity at low theta values as well as diffracted intensity at high theta values, what we will observe? We observe that those radiations which are diffracted at low theta value they have to the diffracted intensity as well as the incident intensity has to pass through a longer distance within the sample, but when you consider the diffracted intensity at a high theta value then we find that the distance travelled by the incident radiation and the diffracted radiation we add up they have to travel much less through the specimen.

So, a in case of the low theta value diffraction, we find there will be more of absorption of both the incident and the diffracted beams by the sample, and if we consider diffracted intensity are at high theta values the total absorption of the incident as well as the diffracted radiation by the sample will be much less. So, simply because of absorption we find that intensity in the high theta of the diffracted beams in high theta region should be more than intensity of diffracted beam at low theta values.

All other factors remaining constant, absorption will cause a higher intensity of the diffracted beam at high theta values.

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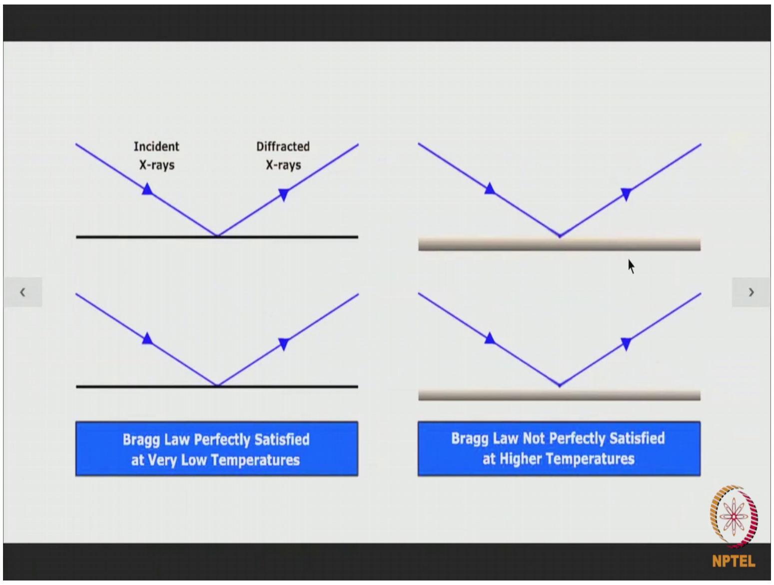

And at a lower value of the diffracted intensity for lines that low theta values. Then comes the temperature factor on the integrated intensity of a diffracted beam in the Debye Scherrer method. Now we consider 2 different cases; one very low temperature situation when the atomic planes are very very narrow they can considered very very narrow because at low temperature, the vibration of individual atoms on an atomic plane will be very very less than in case of a high temperature situation.

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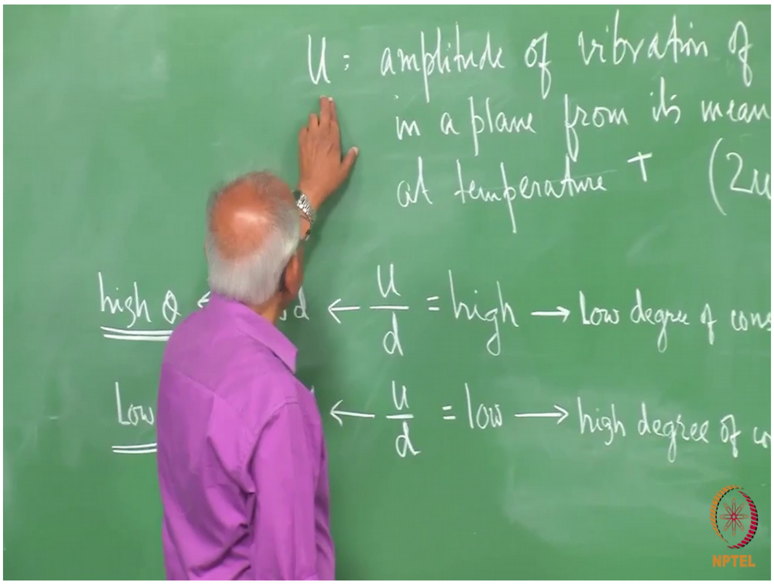

Where because of the high temperature the amplitude of vibration of an atom from it is mean position at the temperature T is same about U; that means, in one case at low temperature the diffraction is taking place from an atomic plane, but in case of diffraction at a higher temperature the atomic plane behaves like a plate, like a plate, like element. So, it is not a simple plane, but you know it is a diffused plane so to say.

Naturally what will happen the Bragg condition will be fully satisfied in this case more less, but the Bragg condition is not going to be fully satisfied in this case because the plane is longer a plane in the orient sense, now the plane is more or less diffused with some amount of thickness attached to it. Now when such a situation arises in general the integrated intensity will be much lower in this case than over here, but the effect of temperature on the integrated intensity is not the same for lines diffracted in the low theta region and the lines diffracted in the high theta region.

Say for example, if u divided by d, d is a interplanar of the plane that I am considering here is very high then what will happen the degree of constructive interference will be low as a result there will be lower integrated intensity in this particular case on the other hand if the ratio u by d is low that will mean high degree of constructive interference of the diffracted rays which will mean higher integrated intensity, but how u by d can be high if d is low and how u by d can be low if d is high now a load, d means we are talking about lines which are getting diffracted at higher theta values because lambda is equal to 2 d sine theta. So, if d is low theta will be high, similarly high d means no theta values. So, what we find we will find that those lines which appear at high value of higher values theta they will be having lower integrated intensity and those lines which are diffracted at lower theta values they will have higher integrated intensity due to the temperature factor.

Now, when we talked about the absorption factor we found completely the opposite situation, there we found that absorption will be much higher in the low theta detection. So, as a result integrated intensity will be lower here.

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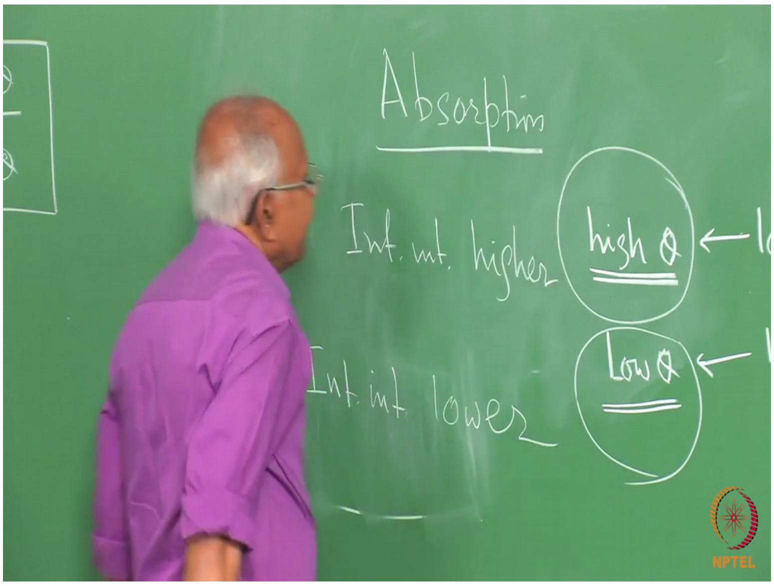

So, integrated intensity will be lower in this particular case, and on this side on the high theta region absorption is less. So, integrated intensity is higher.

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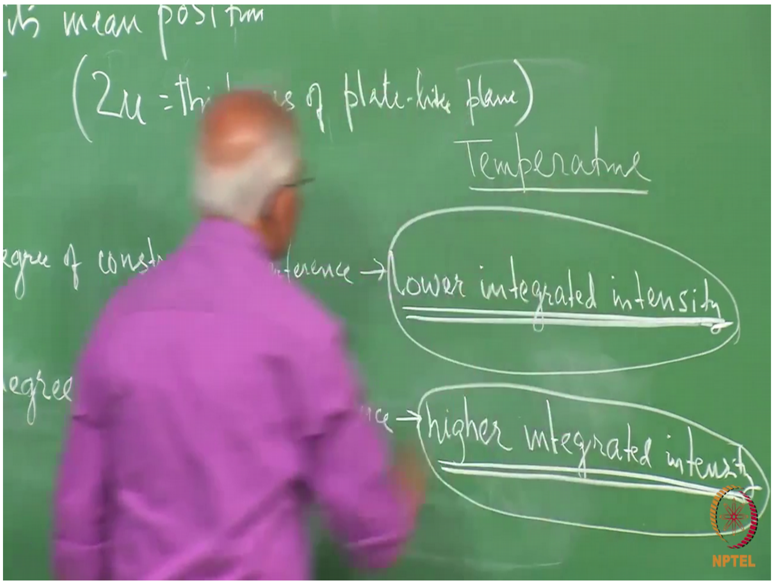

So, this is due to the absorption in the specimen and this is due to the temperature factor. So, due to absorption high theta lines their intensity will be higher low theta lines their intensity will be lower and due to high temperature high theta lines will have lower intensity and low theta lines will have higher intensity.

So, we say that the effect of absorption is very worse of the effect of temperature, and since it is very difficult to calculate the exact effect of absorption as well as temperature. So, for as the integrated intensities concerned, we assume that the effect of one nullifies the other. So, when we determine integrated intensity from a diffraction line we do not consider absorption factor and the temperature factor at all.

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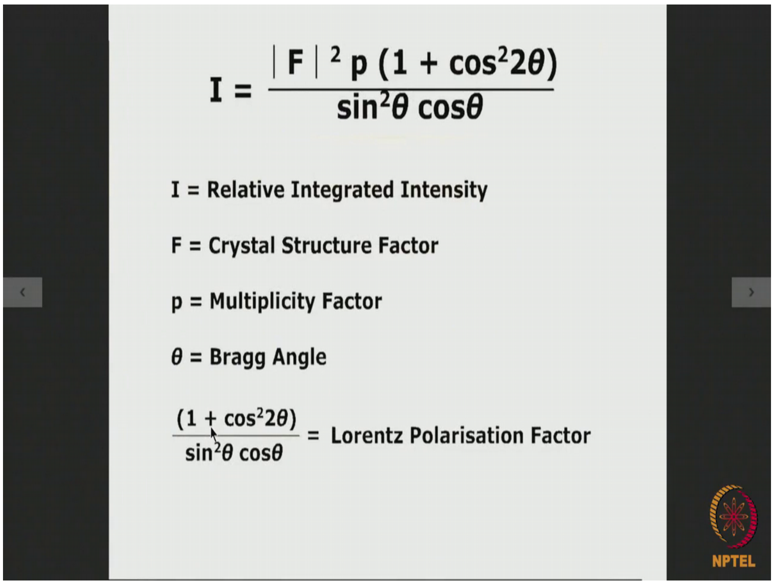

$$I = \frac{|F|^2 p\,(1 + \cos^2 2\theta)}{\sin^2\theta \cos\theta}$$

I = Relative Integrated Intensity

F = Crystal Structure Factor

p = Multiplicity Factor

θ = Bragg Angle

$$\frac{(1 + \cos^2 2\theta)}{\sin^2\theta \cos\theta} = \text{Lorentz Polarisation Factor}$$

So, now, for a Debye Scherrer method the integrated intensity or the relative integrated intensity can be written by this expression where F square this is the square of the crystal structure factor, we know that crystal structure factor is an amplitude. So, square of that is intensity. So, that is why this will appear in intensity equation of the F square. P is a multiplicity factor. So, if for a particular plane multiplicity is higher then it will show a higher intensity, if for a diffraction line for which the multiplicity factor is lower with lower intensity.

And what about the 1 plus cosine square 2 theta divided by sine square theta cosine theta this is the Lorentz polarization factor. Now we have left out the temperature factor and the absorption factor from the intensity equation because as I already mentioned the effect of the other is exactly the opposite of the effect of the effect of one is exactly the opposite of the effect of the other. Therefore, we can say that if we want to find out the relative intensity of a diffraction line in the Debye Scherrer method it can be given by an equation of this type. Now things are complicated in case of the related intensity of diffraction lines as we find for in case of a diffractometer.

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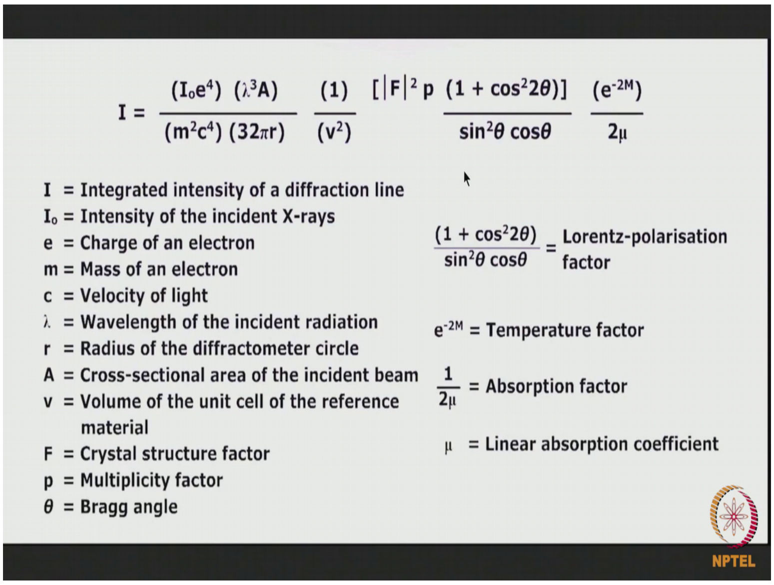

$$I = \frac{(I_0 e^4)\ (\lambda^3 A)}{(m^2 c^4)\ (32\pi r)}\ \frac{(1)}{(v^2)}\ \frac{[|F|^2\, p\ (1 + \cos^2 2\theta)]}{\sin^2\theta\, \cos\theta}\ \frac{(e^{-2M})}{2\mu}$$

I = Integrated intensity of a diffraction line
I_0 = Intensity of the incident X-rays
e = Charge of an electron
m = Mass of an electron
c = Velocity of light
λ = Wavelength of the incident radiation
r = Radius of the diffractometer circle
A = Cross-sectional area of the incident beam
v = Volume of the unit cell of the reference material
F = Crystal structure factor
p = Multiplicity factor
θ = Bragg angle

$\frac{(1 + \cos^2 2\theta)}{\sin^2\theta \cos\theta}$ = Lorentz-polarisation factor

e^{-2M} = Temperature factor

$\frac{1}{2\mu}$ = Absorption factor

μ = Linear absorption coefficient

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So, here the expression is I integrated intensity or the relative integrated intensity is equal to I 0 e to the power of 4, lambda cube a m square divided by m square c 4 into 32 pi r whole thing by 1 by v square and s square p, 1 plus cosine square 2 theta sine square cosine theta e to the power minus 2 n and 2 mu.

Now I is a integrated intensity of diffraction line I 0 is the intensity of the incidence X rays e and m are the charge and mass of an electron c is the velocity of light lambda is a wavelength of the incident radiation small r is the radius of the diffractometer circle, a is the cross sectional area of the incident beam, small v is the volume of the unit cell of the reference material we are examining, f is a crystal structure factor, p the multiplicity factor, theta the Bragg angle and plus cosine square 2 theta by sine square theta cosine square theta is the Lorentz polarization factor this factor e to the power minus 2 m we are not explicitly written what is it all about is a temperature factor, and 1 by 2 mu is a absorption factor where mu is nothing, but the linear absorption coefficient.

So, we say that depending on which kind of method we are using it is possible to find out the relative integrated intensity of all the diffraction lines that appear in the pattern of the material.