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Lecture-32
Materials Characterization
Fundamentals of X-ray diffraction

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Hello everyone welcome to this material characterization course. In the last class we just looked at the X-ray diffraction and its application to the crystal structure determination. And we looked at the crystal size. How it is being determined by the X-ray diffraction, and also we have seen that the effect of the strain. And how to determine that through X-ray diffraction and importantly. We just looked at how to separate these two effects that is the crystallite size effect as well as the strain effect through Williams and Hall plots. And in today's class we would like to look at some of the other important applications such as the determination of the crystal structures.

And then face identification one of the most important applications of X-ray diffraction and most of us find it very useful in material science. And engineering and finally we will look at most industrially important application of X-ray diffraction. That is the stress measurements so we will look at the very basic principles of all this applications in this general course. And we will not get into the very detailed about the each aspects because each one of them will have its phone will be dealt with a very in a broad manner in a specialized course. So in the today's class we will start discussing about the determination of the crystal structures using X-ray diffraction.

So if you recall the earlier lectures what we have talked about the, the intensities X-rays intensities. And how they contribute to that I mean the arrangement of atoms and so on. When we look at the reciprocal lattice concepts and so on. Just recall those things and then we can

broadly I mean classify some of the basic ideas which behinds that I mean which determines the total integrated intensity of the X-ray diffraction.

If you look at it from the basic aspects of X-ray diffraction the crystal I mean cysts crystal structure determines the type of diffraction pattern. And the shape and size of the crystal, crystal system determines the angular positions of this diffraction pattern. And if you look at the number of atoms and its arrangement determines the total intensity of the X-ray diffraction pattern. So but broadly what we can do is we can just make a small table to illustrate this aspect.

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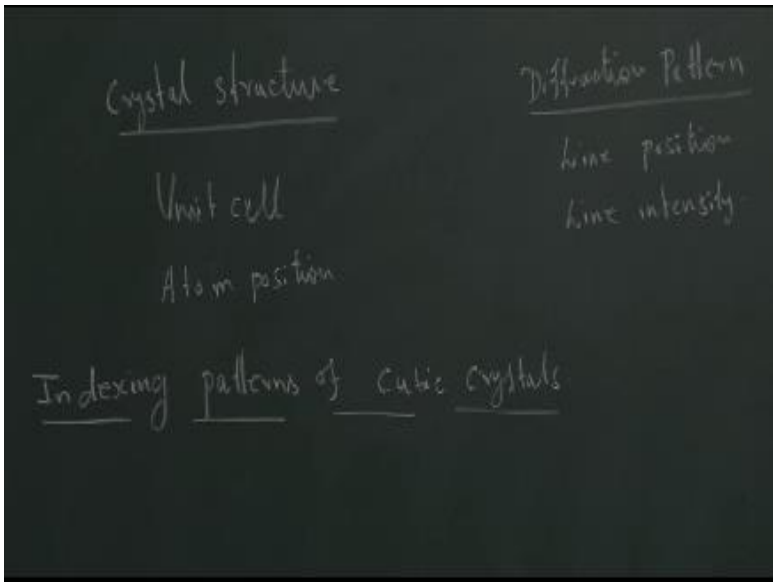

For example if you can write like this a crystal structure at one end. Where you have the unit cell and item position on the other hand you can write a diffraction pattern. So what you can just look at it this unit cell determines the line position of the diffraction pattern the atom position determines the, the integrated line intensity. So this is some of the basic aspects of X-ray diffraction and its intensity related to the crystal structure. But commonly we are interested in determining the unknown crystal system. The most popular method of determining the, the crystal system is through a sine squared θ measurements.

And I would like to just caution this, this particular measurement of sine squared θ depending upon the type of the diffract meter one uses. So one has to take care of the correction of the sine square θ and then it varies with methods two methods. We will not get into the details but I will just briefly discuss how this sine square θ is going to be used to in determining the crystal structure especially the cubic system. Which is a simplest system you will understand and from there we can extend it to a few more other crystal system. And then you can realize how it is useful and in determining the particular crystal system.

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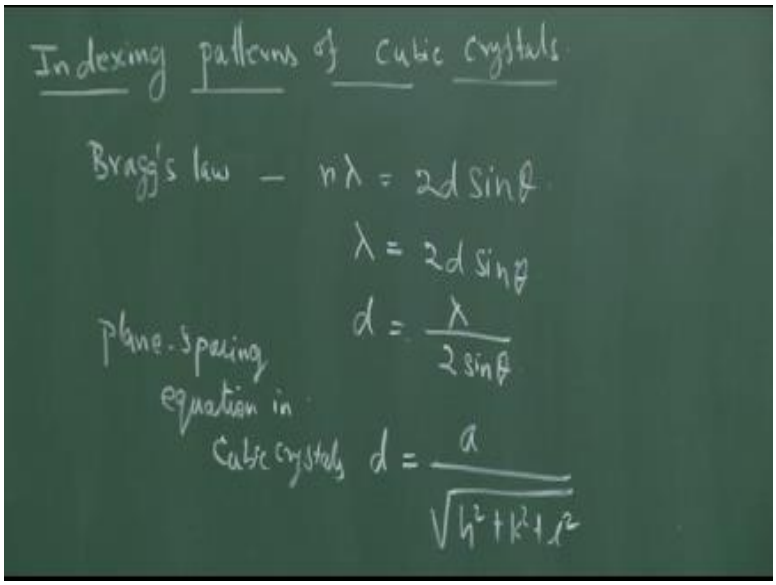

So we will take a one particular example first we will talk about indexing the patterns of the cubic crystals and. Where you have the two important law or you can generally it is written like this you have Bragg's law N λ= D sine θ. It mode generally written as λ = 2D sine θ. And you can also write D = λ applies to sine θ. Can write like this and the plane spacing equation in cubic crystal that also you can use it that is D= A/square root of $H^2 + K^2 + L^2$. If you look at these two durations where you have D = λ x 2 sine θ. And for a cubic crystal this relation is valid.

Now we can have a common relationship between these two and then we can write a 1 expression for a sine squared θ. And then side that sine squared θ is the value. Which we which

is going to be most useful to over calculations. So let us see how what is that relation so you write like this.

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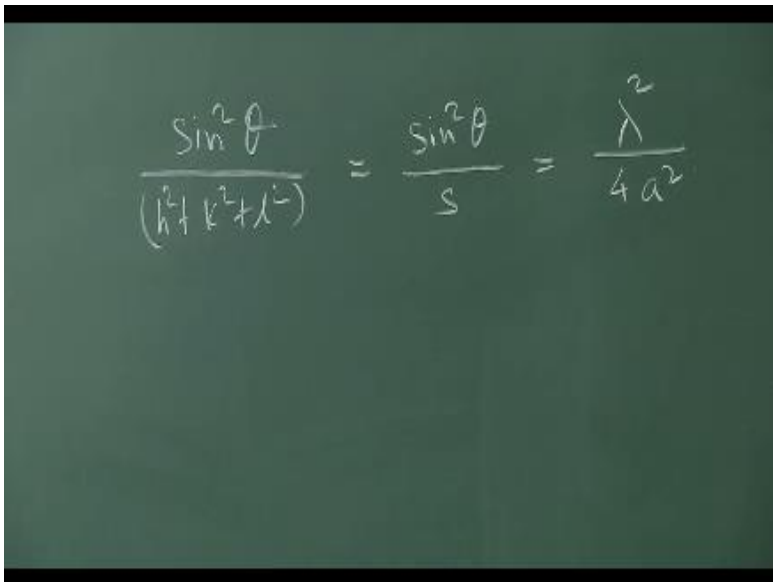

So you can write from this two equations sine square θ / $H^2 + K^2 + S^2$ which is written as sine squared θ by S which is equal to λ^2 / 4 A^2 here.

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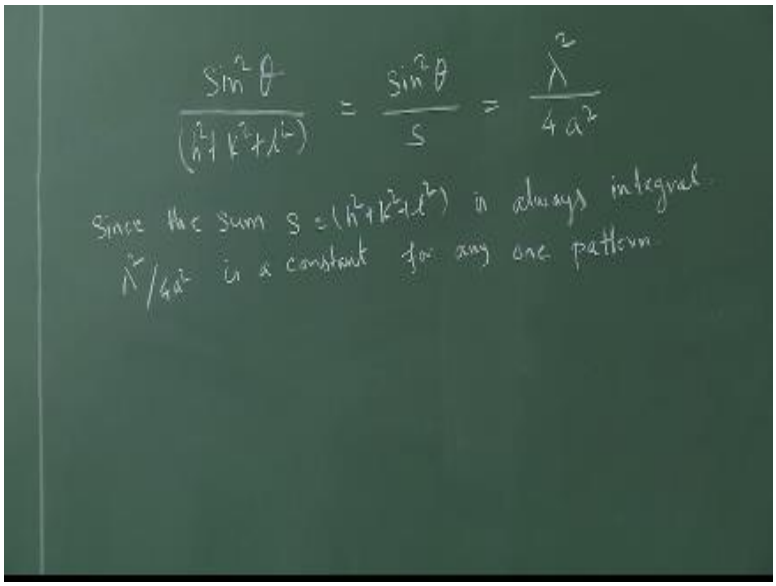

We can write this some $H^2 + K^2 + L^2$ are always an integral and then the $\lambda^2 / 4A^2$ is a constant. Since this is a constant now we have to find the, the integers which will have you know the some of the relations with this sum, sum of the integers we have to find which will satisfy this. Let us see how we can do that.

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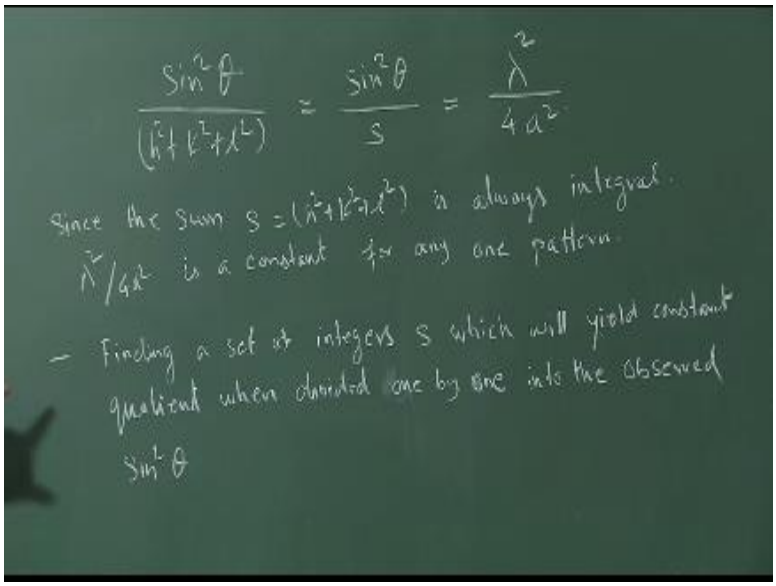

So what I have written is the aim is to find out a set of integers S which will yield a constant quotient when divided one by one into the observed sine squared θ value. So what you observe from an experimentation is a sine square θ value and then from there using this relation. We can find out a set of integers which will eat the quotient. So what are those in set of integers that is the question so we will now find for a simple cubic.

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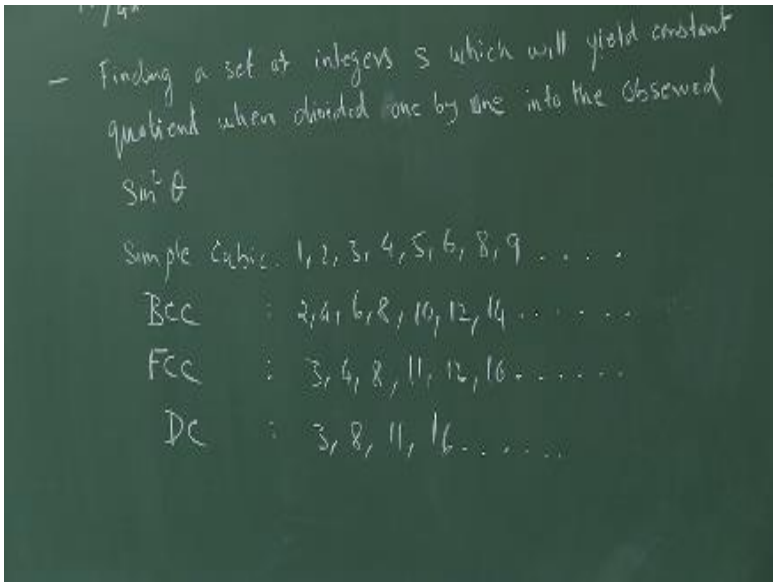

So look at these numbers for a simple cubic system these are the, the integers which will sum up some of this $H^2 + K^2 + L^2$. Which will follow these coefficients will be allowed reflection or whatever it from the cubic system so that is 1, 2, 3, 4, 5, 6, 8, 9 and this is for a body centered cubic system 2, 4, 6, 8, 10, 12, 14 and so on. And this is a face centered cubic system 3, 4, 8, 11, 12, 16 and so on. And finally this is for a diamond cubic system this is 3, 8, 11, 16, and so on. So you should notice that some of the numbers are missing some, some numbers are missing in this series for example you can write certain integers.

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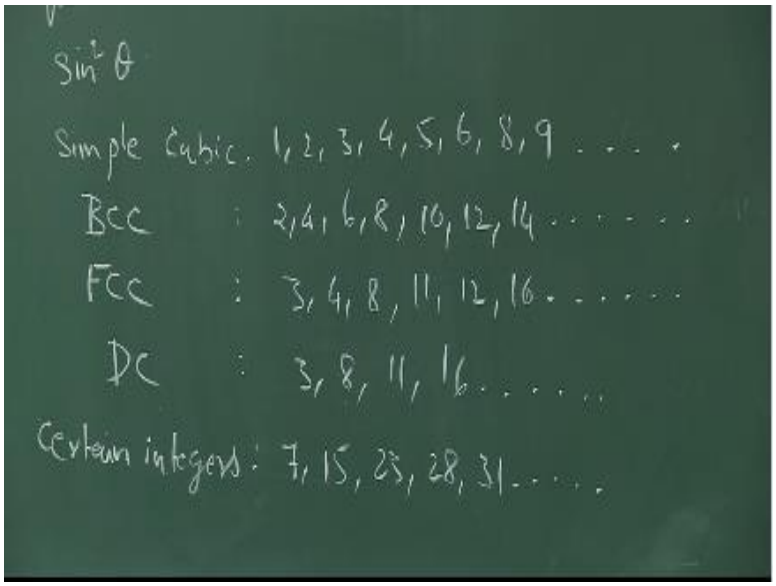

Such as 7, 15, 23, 28, 31, etcetera will not find in this series because the sum will not yield these kind of and numbers. So these are all rolled out from this series and then you can actually make a table for a observed sine squared θ value. You make a table and then put as a S in one column and you have put all the system in the other column whichever it is allowed. And then we can tabulate it and also you can tabulate the sine squared θ value. And that is how the, the crystal structure is determined using sine squared θ for a simple cubic system. Now we will look at another simple system called as you know tetra colonel system how it is done.

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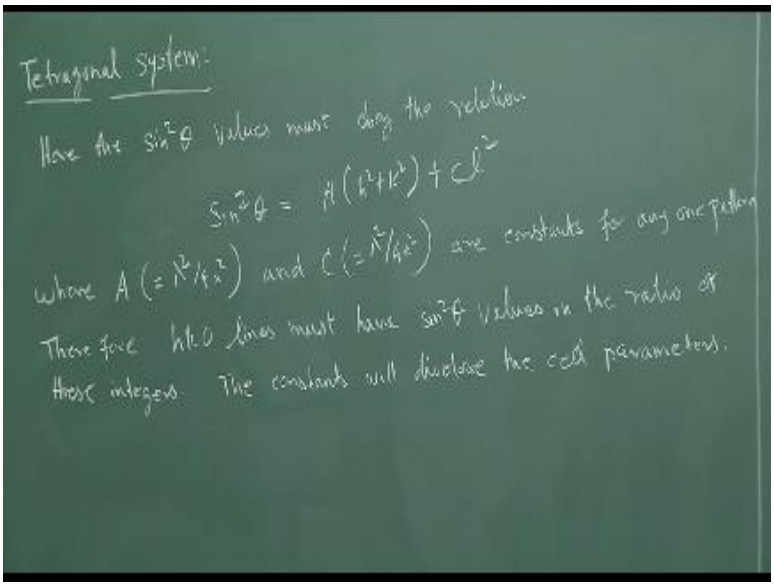

Here the find out the sine squared θ radiation which is so you have sine square θ is equal to A into $H^2 + K^2 + CL^2$. This is a relation for tetra Grinnell system so how to find out the crystal structure from this relation. So let us look at we can write where A which is a constant again and see it is a constant for any one pattern. And then we can find out therefore HK0. So you should also know why we are interested in these constants apart from the finding of the integers.

This will satisfy this sine squared θ relation. These constants will disclose the cell parameters ultimately our interest is to identify the crystal system. So the finding out the constant is also very important you will now see how to find out the constants first and then we will move on to the selection rules. So in order to find the A let us see that the value of A.

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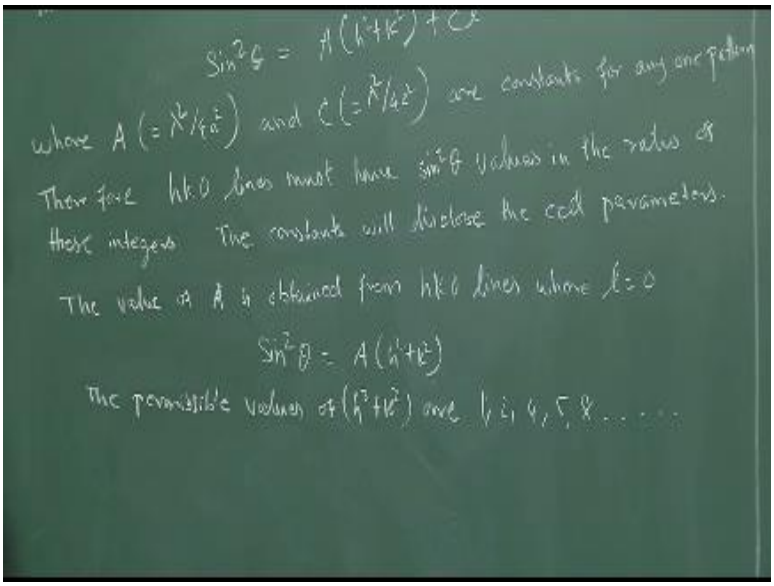

So that means if you put L =0 here then your equation is modified like this. Now you see that the permissible you so once you have this then we can say that the HK0 lines must have a sine square θ values in the ratio of this integers. Then we will be able to find this value of the constant now the C is the value of C is obtained.

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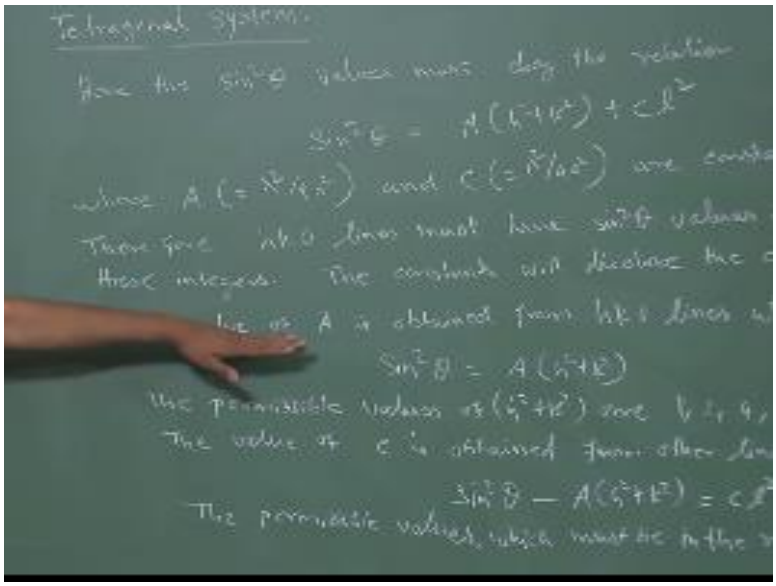

From other lines which will use this relation so the permissible values which must be in the ratio 1, 4, 9, 16, etcetera. So once these values are found out and your C can be calculated similar to what we have done it for A. So like that we can go ahead with the other systems also for example hexagonal system and monoclinic and try cleaning system.

The only problem is the, the more the crystal system becomes a symmetric for example triclinic and monoclinic the number of constants. That is whatever we are seeing A and C it will become meaning if you have many constants. Then a manual calculation becomes tedious and you require a special computer programming. And these are available in fact when I show the laboratory demonstration I will show how these calculations are done using and software automatically.

So I will not go into the other systems now I will go to the other applications which I talked about is the face identification by X-ray diffraction. See this is again a one of the important application of X-ray diffraction especially when you have the phase mixture. Suppose if you have two three phases in a mixture how to find out the phase what is the phase and how to identify them that is the challenge. So one of the easiest method of finding out this by X-ray

diffraction and if you recall the, the earlier discussion on X-ray I mean X-ray diffraction and it is integrated intensity.

You have to think about a qualitative I mean if you want to do it at quantitative rather than qualitative assessments you have to calculate Lee calculate the integrated intensity. And then the integrated intensity it depends upon several factors. If you, you have to recall those aspects and then we will discuss what is that the starting point of the problem. How to solve this problem?

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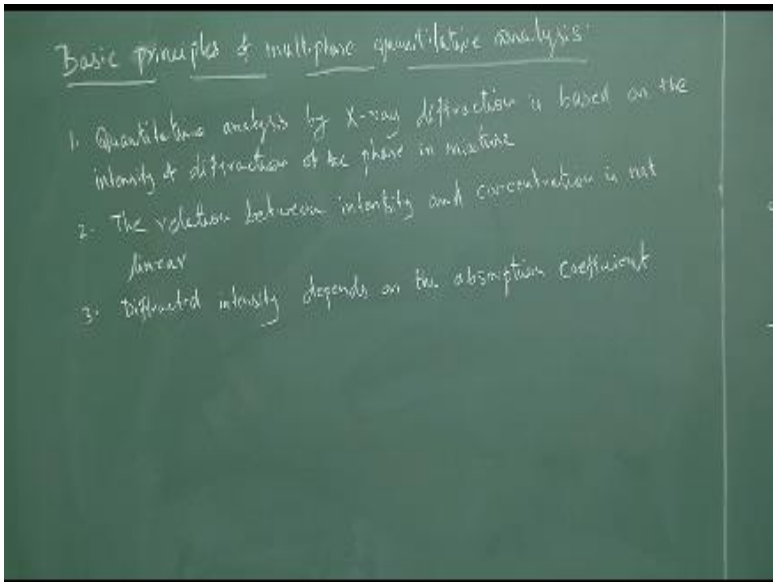

So you have to understand the three important points before we look into this quantitative analysis of multi-phase materials. What is the basis the quantitative analysis by X-ray diffraction is based on the intensity of a diffraction of a particular phase of the interest in a mixture? And that intensity of diffraction in turn depends upon the concentration of the particular phase in the mixture that is the second point important points the, the problem is the relation between the intensity and the concentration is not linear always. And then the defective intensity depends motley markedly on the absorption coefficient which in turn will vary with the concentration. So these three points you have to keep in mind.

So the in order to identify the face from the next ray diffraction the starting point is the intensity equation if you recall we have written a very long intensity equation. I will just write it for the reference you know the meaning of all this term which we have already looked at in the earlier class just for the sake of completion I will rewrite those things.

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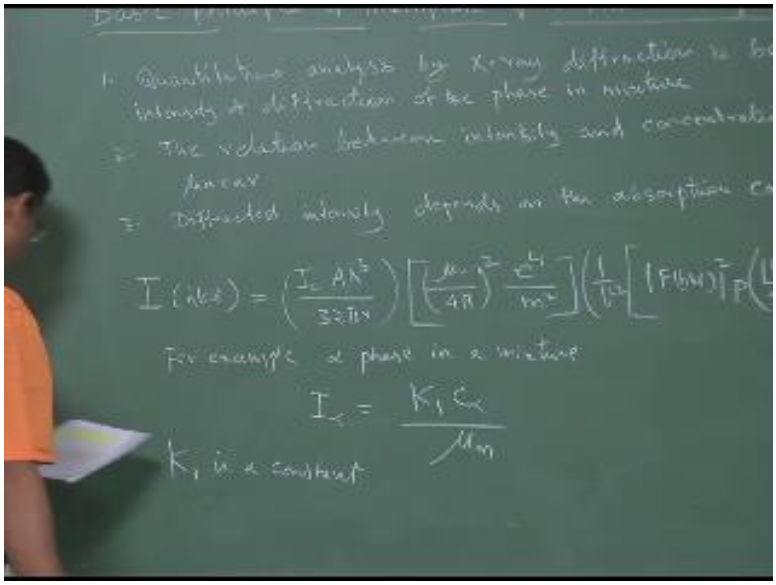

And you will appreciate what are the terms which we need to really bother about. So this is the expression for an integrated intensity for a given HKL plane. We have already looked into what is the meaning of all these terms. And you are much familiar with that now how do we this is the starting point the problem with this expression is this is applicable for only the pure substance. And then we have to convert that into an easier form where we can simply adopt this intensity for the two phases or a multi phase mixture or a component.

So how do we do that so we can write everything for example, I will write it for a two phase a mixture or a multiphase mixture where I am interested in the phase α, α phase in a mixture then I will write this expression like this I α is equal to k1 Cα this is absorption coefficient so the multiplication of Cα is required here because the concentration of the α which is responsible for

the diffraction intensity which is much lower if it were to be completely from α alone but now it is from the mixture so this is has to be written like this.

And then we can now write K_1 is a constant and which is unknown K_1 is a constant which is unknown because and generally I_0 is also unknown but we do not have to worry about this it becomes unimportant if you take a ratio of two in ten cities one from the standard one is from the unknown if you take the ratio then we do not have to worry about this that constant so that is the idea so now let us see how we can rewrite this.

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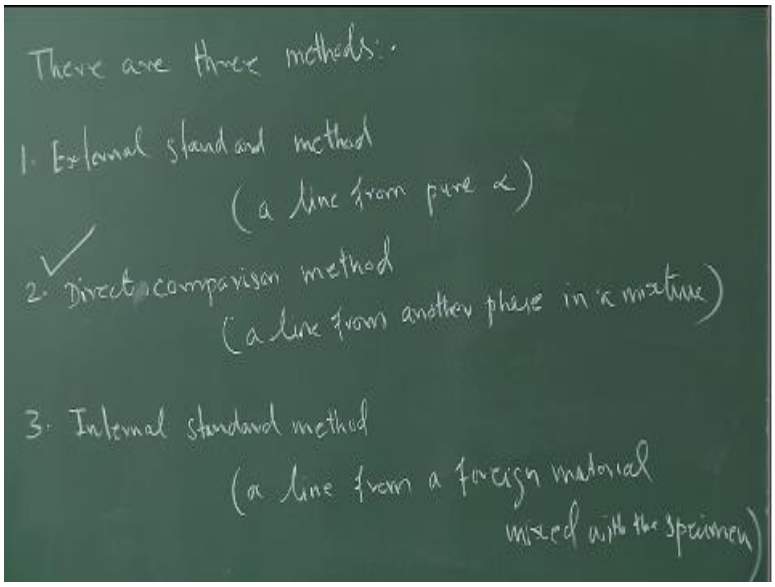

Okay before I get into the example there are three methods so before we take up this kind of neat expression and then look at the ratio in identification of the unknown we would look at the what are the general methods available for doing this quantitative analysis one is external standard method where a line from a pure alpha is being used and you have direct comparison method where a line from another phase in a mixture is used internals standard method a line from a foreign material mixed with the specific.

So these are the three standard methods which is used in the quantitative analysis of multi-phase materials or a mixture we will take up this particular technique that is direct comparison method and then we take up a two-phase mixture and try to identify how to calculate the concentration of an unknown phase from this intensity expression see I will just make it more general normally in a metallurgical system or material science system a steel is taken as an example where you have a mountainside + austenite or Austin I + ferrite kind of a mixture where people are interested in finding out the austenite fraction which is industrially more important .

The people who like now I will not insist on that I will make it more general because the people do not have the materials background you can assume that in a two-phase mixture like α and β where you can consider are a γ and α whatever it is we're one of the fraction phase fraction is which is less but still we want to quantify them to x-ray diffraction and this method can be adopted so now we will rewrite this expression in order to get this two phase mixture calculations.

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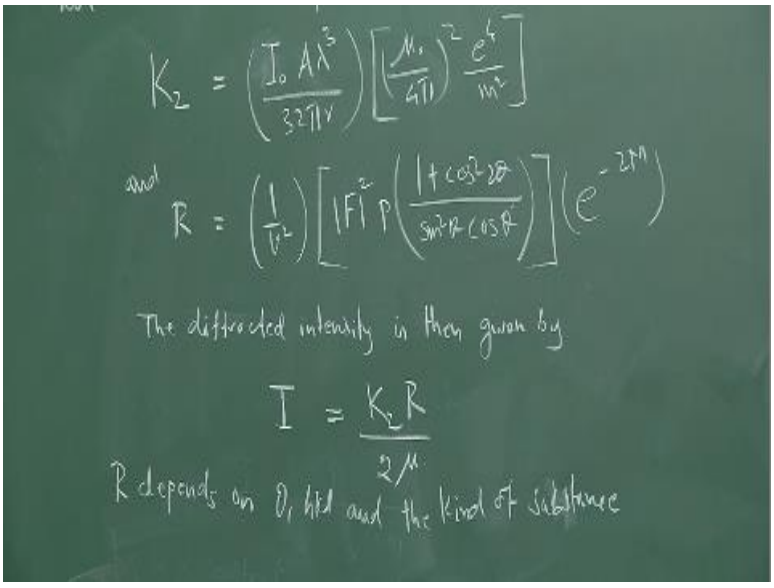

So let us take a two phase mixture with γ and α and also assume that γ and α have a two different crystal structure then in that case we can write this intensity expression in this form you carefully

observe here what we are doing see you have now separated the integrated intensity into two forms one is K_2 and another is R where K_2 is a constant which is independent of the substance but are using different on θ HKL and kind of substance and so on. So we have separated the terms into two different constants and then we have written the defected intensity in this form is equal to K2 times or divided by 2 μ.

So we can write that for reference or depends on θ HKL and kind of substance, so now we will rewrite this or adopt this expression for the two phase mixture γ + α so you write Iα.

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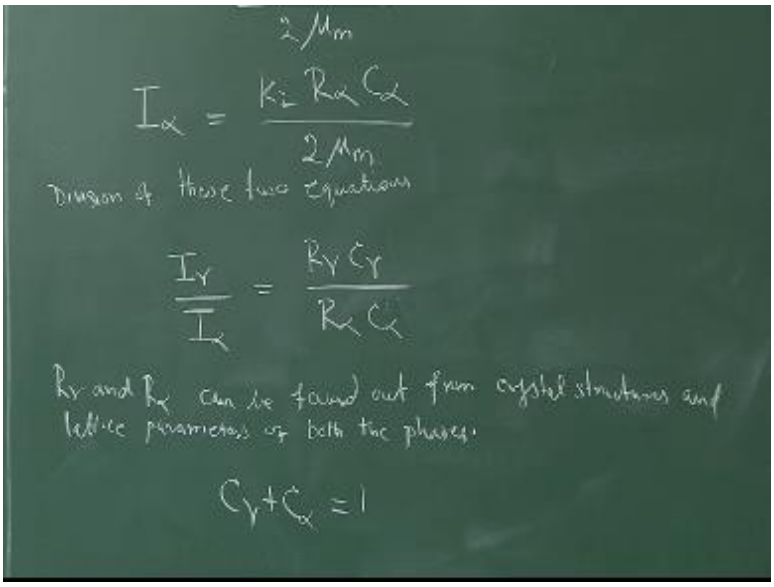

Iγ is equal to K2 is a constant anyway or depend on θ and HKL so we will say Rγ and we are interested in finding out concentration of this phase so Cγ so divided by your mass I mean absorption coefficient this is for one phase and this is for then another phase we have Iα so similarly you right k to our alpha and Cα which is in the mixture and then you can write like this so division of this two equation yields so you write Iγ by Iα which is equal to Rγ Cγ divided by Rα Cα and Rγ and Rα can be found out from the crystal structures knowledge of crystal structure and lattice parameters.

And once you know this Rγ and Rα we will be able to find out the concentration of the unknown from this relation because it is two phase mixture and once you know the R then you know this ratio so you know the Cα you will be able to find out Cγ from this relation so that is how the direct comparison method is used to identify the one of the face in the phase mixture namely γ and α suppose if you have one more unknown component the constants becomes suppose Rγ Rα Rβ and if you find out that you will also be able to calculate from this relations.

For example is equal to 1 suppose if you have one more phase which requires then those things also can be identified through these kind of calculation with the ratio method so this is very simple and straightforward method and very effective and mostly widely used relation in the material science so the final application I would like to show is stress measurements is another very important area in the in terms of an engineering components and it has got more element industry and the we will discuss the basic principle behind measuring the stress in a component by x-ray diffraction so we will just draw some schematic quickly and then we will take it from there.

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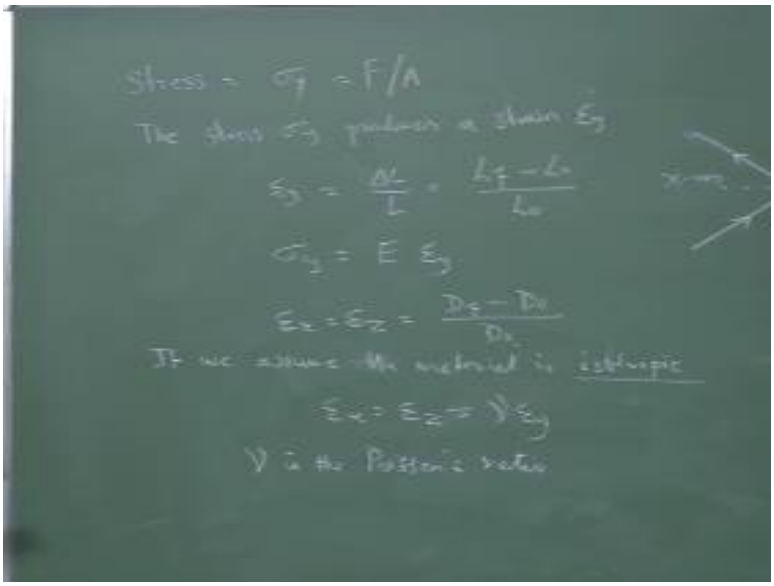

You so this is the coordinate axis towards the perpendicular to the blackboard this is Z and this is why and suppose you assume that this is a x-ray which comes and we are trying to identify assume that this is a cylindrical sample which is being pulled in the uniaxial direction and you have the dimensions of d and l and this is the x-ray which comes and impinges on the surface of the sample and then it get diffracted so how are we going to use this geometry for identifying the relation so we will light the basic expression or stress.

Is equal to σy here because these are Y direction so we write like this force by area in the y direction and you assume that there is no force in the X and Z direction so for this we can write some relation the stress yY produces the strain epsilon y and which is given by epsilon y Δ l by l which is nothing but L final - L initial / Elmo this is a original length this is after you stretch it and then you get the strain and this strain is related to the stress by this is very famous Hookes law so the stress is related by strain by this relation and we can also relate this E_x in E_y Z is equal to D final - D initial divided by $V_{0.}$

So this is the strain in the X Direction strain and is that direction is measuring by this change the final - D initial by b naught which is a diameter of the sample also can be represented by this if the if we assume that material is if you assume that the material is isotropic then we can write epsilon X is equal to E_x is equal to mu time E_y this is also true where μ is the fashion section so now how this relations are related to our x-ray diffraction that is the idea.

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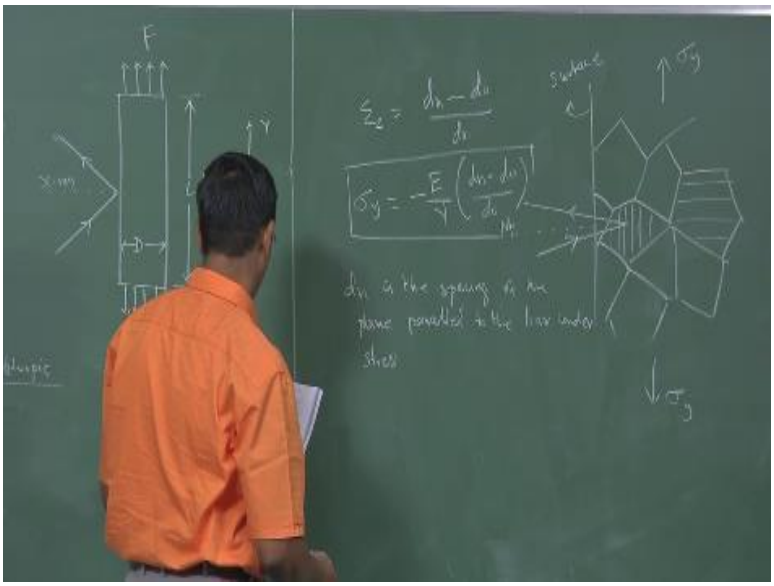

I have to write one more schematic quickly putting direction the B spacing is smaller compared to the planes which are perpendicular to the loading axis you can see the distance is different because of the stress so this is the bottom line this is the bottom line for using the x-ray diffraction so we can quickly look at epsilon Z is equal to $d_n - d_0$ divided by d_0 so this is your initial d spacing this is normal the after the stress then what is the B spacing so that is the difference so we can write σy is equal to - e divided by Q where $d_n - d_0$ by d_0 so this is this is the relation which forms the basis for this using x-ray diffraction.

You find the d spacing and I will write the details d_n is the spacing of the plane parallel under stress so DNS under stress and D d_0 is about stress so you see that difference and I think this is the basic idea behind the measurement of stress using x-ray diffraction you will be able to identify the d spacing and you have to remember that you have to have the plane always perpendicular to the this is a normal plane where NP is the x-ray diffraction takes place where the plane which are perpendicular to this incident.

So you have you have to make sure that this kind of informations are always obtained only from the plane which are parallel to this loaded or perpendicular to this load axis or I would say

parallel to the x-ray diffraction and soon so you have to keep that in mind and in fact this is what we are talking about at a simple case actual cases a biaxial and try axial stresses are measured with an elaborate procedures involved and people calculate the residual stress which is a very important component in engineering application and we can readily quantify these stresses using x-ray diffraction.

Similar based on the fundamental principles like this so we will not get into the details because each one will combine a special course in itself but as a beginner you should know what is the basis of x-ray diffraction in use in applying for all this parameters like you know crystal structure determination face identification stress measurements and so on so in the next class I we take you to the lab and then show actual how we measure this in a material in a polycrystalline material how do we obtain an x-ray data and.

Then how do we analyze with the interface a software today and everything is automated so you just get the final result in your desktop but you have to understand unless you get into this fundamentals here then you only you will be able to appreciate what the software is doing in your interface so that is the intention of this particular I mean illustrations what we have shown today's class so we will see you in the next class with the demonstrations thank you.

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