X-Ray Crystallography

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Lecture - 17
Determination of Crystal Structures

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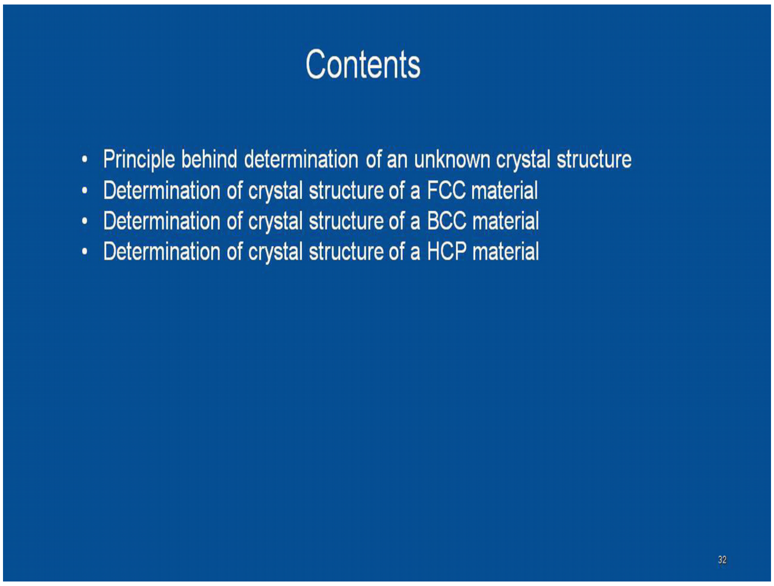

Now, that I am finished with the fundamentals of X-ray crystallography. I shall concentrate on various important applications of X-ray diffraction. The reason why we must have diffraction from a material when an X-ray beam is incident on it is a fact that we must have some information out of that material or that crystal in the form of a diffracted beam that will contain all the information that there is to see within the crystal or within the material.

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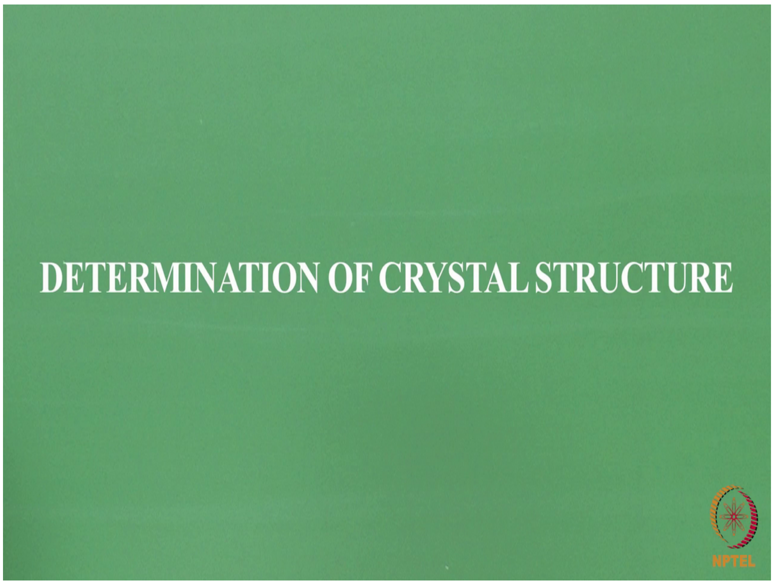

Now one of the most important applications of X-ray diffraction is the determination of crystal structure. For this purpose what we do is we index a diffraction pattern. So, what is meant by indexing? By indexing you mean we look at all the diffraction lines in the pattern determine the h k l values of all the planes that give rise to the diffraction lines, determine the crystal structure at the brave lattice from these diffraction lines. And finally, also determine the lattice parameter or parameters very precisely.

Now normally when we do a diffraction analysis from an unknown sample just by looking at the diffraction lines and their positions and their intensities?. It is in most cases not possible to figure out which crystal system the material belongs to. So, in a way we can say that determination of crystal structure of an unknown material is more or less a trial and error method.

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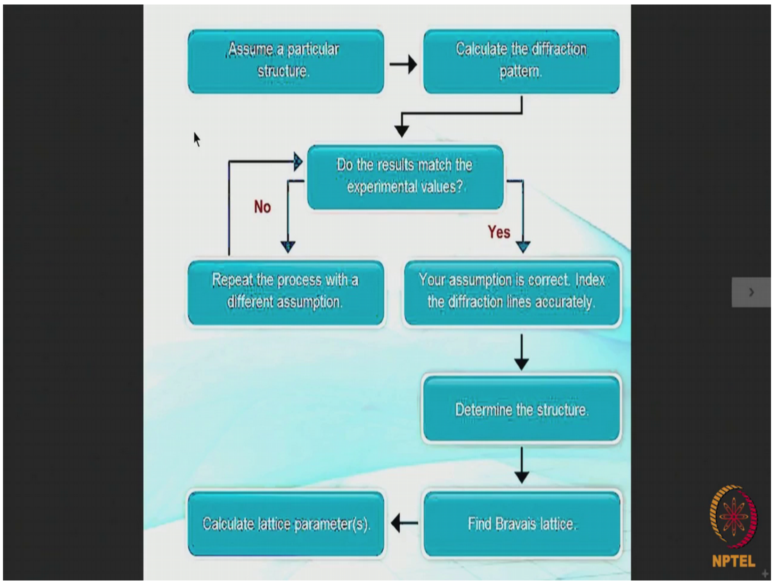

For example: when we do a X-ray diffraction from a particular material we get the diffraction data in the form of diffraction lines. We initially assume a particular structure for the material in an intelligent way. Then, from there we try to calculate what should be diffraction pattern like. Then, we find out if the results match the experimental values; if yes, we can be assured that our assumption is correct. Then we start indexing the diffraction lines accurately from there we determine the crystal structure find out the brave lattice and then calculate the lattice parameter or parameters.

If on the other hand we find that the calculated diffraction pattern does not match the experimental values then we repeat the process with a different assumption. Now here I shall discuss how to determine the crystal structure brave lattice and lattice parameter from the X-ray diffraction lines of an FCC material a BCC material and an HCP material.

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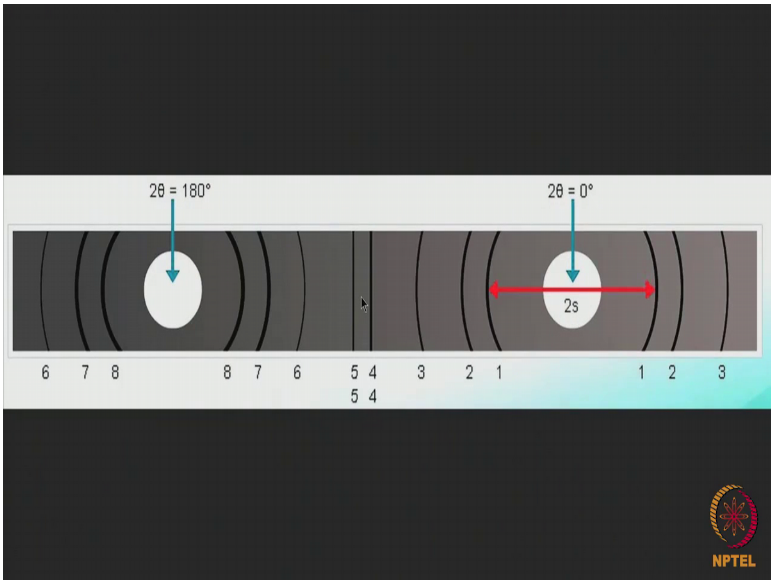

Say for example: this is an XRD pattern of an unknown substance. Now to begin with we assume the simplest possible crystal system for this material which is cubic. So, we assume the material has a cubic crystal structure. Now the first thing to do is to determine the distance between each of the line pairs which appear on the diffraction pattern.

Say this is the line pair 1 1 coming from a particular diffraction from a particular h k l, then this two are the 2 2 line pair which appear due to diffraction from another particular h k l plane. This is a 3 3 line pair which is due to diffraction from a third h k l plane, etcetera, etcetera. So, the first thing to do is to measure the distance between the any line pair.

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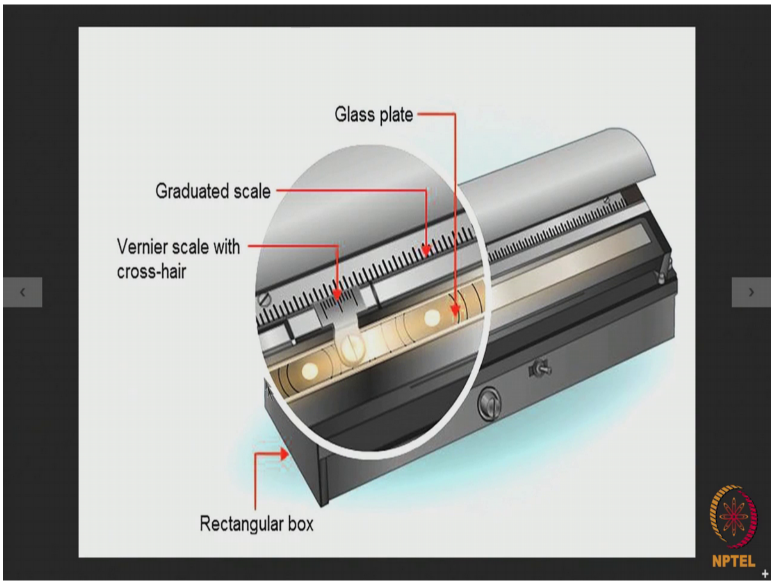

So, this we do using a rectangular box of this type which has got a glass plate here below which there is a source of light so that all the lines all the patterns are shown very clearly. There is a graduated scale along with a vernier in order to measure the line positions very very accurately.

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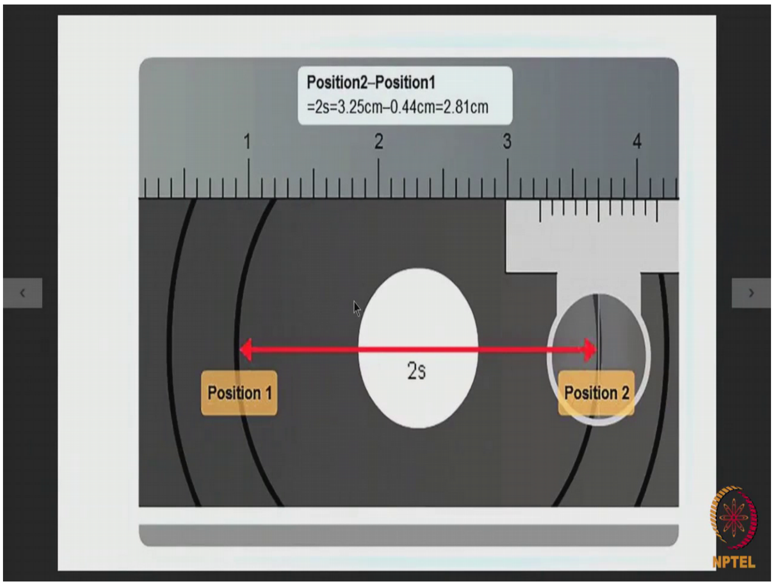

Say for example: this is my line pair 1 1. So, this is the position 1 for this line pair, this is the position 2 of the line pair. We find out with the help of the scale and the vernier what are the values here and what are the values there, and then we subtract one from the other. So, in this way we find out that this value 2 S for this line pair is simply equal to 2.81 centimetre c m.

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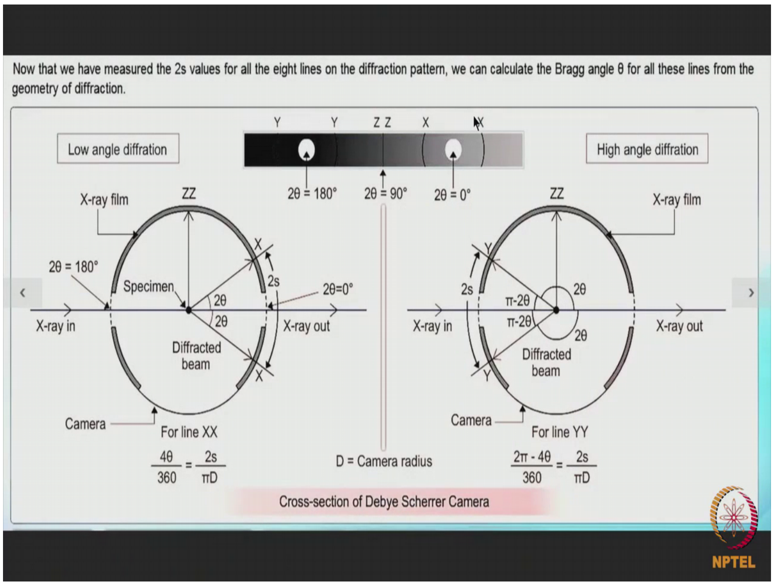

Now, if we recapitulate what we did in case of description of the Debye Scherrer method if we choose a low angle diffraction line say the plane the plan is given raise to the diffracted beams over here. So, this distance on the film is the distance 2 S as we have always seen now we can easily write this length which is 2 S divided by this circumference which is pi times d these are diameter of the camera here there is a mistake it is camera diameter not camera radius. So, 2 S divided by pi d will be equal to the angle subtended here is 4 theta and the angle subtended the whole circumference is 360. So, from this relationship since d is known the camera diameter is known S has already been measured we can find out the value of theta for this particular line in this way for all the low angle diffraction lines we can measure we can find out the corresponding theta values corresponding values of the Bragg angles.

Now, if we are looking at a high angle diffraction line on this side then say this is where the high angle diffraction lines are found for a particular atomic plane. So, since this is the X-ray in direction and this is the direction of diffraction this will be 2 theta as a result this angle will be pi minus 2 theta this angle will also be pi minus 2 theta. So, if we measure the distance between this line pair if it is 2 S and if we divide it by pi d. So, it will be equal to 2 times pi minus 2 theta which is 2 pi minus 4 theta divided by 3 hundred and 16 from this relationship since S has been measured and since d is known we can easily find out the value of theta the Bragg angle.

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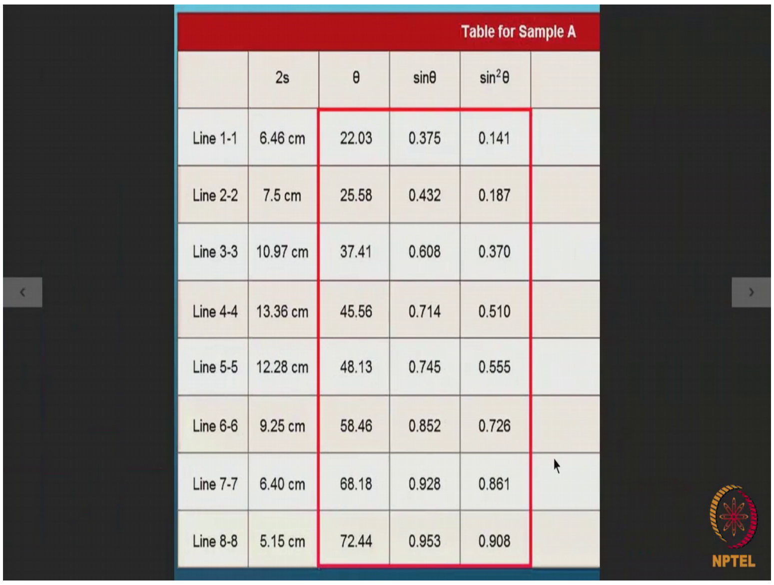

Table for Sample A

	2s	θ	sinθ	$sin^2θ$	
Line 1-1	6.46 cm	22.03	0.375	0.141	
Line 2-2	7.5 cm	25.58	0.432	0.187	
Line 3-3	10.97 cm	37.41	0.608	0.370	
Line 4-4	13.36 cm	45.56	0.714	0.510	
Line 5-5	12.28 cm	48.13	0.745	0.555	
Line 6-6	9.25 cm	58.46	0.852	0.726	
Line 7-7	6.40 cm	68.18	0.928	0.861	
Line 8-8	5.15 cm	72.44	0.953	0.908	

So, in this way for all the lines in the pattern whether in the low angle side or in the high angle side we can find out the value of theta the Bragg angle say for the particular case we have 8 lines and say we have measured all the 2 S in this fashion from which I can find out the value of theta for each line pair.

I can find out the value of sin theta for each line pair I can find out the value of sin square theta for each of the line pairs. So, to begin with we assume that the material has the simplest crystal structure say cubic now if we have a cubic material the relationship between the interplanar distance of a set of planes.

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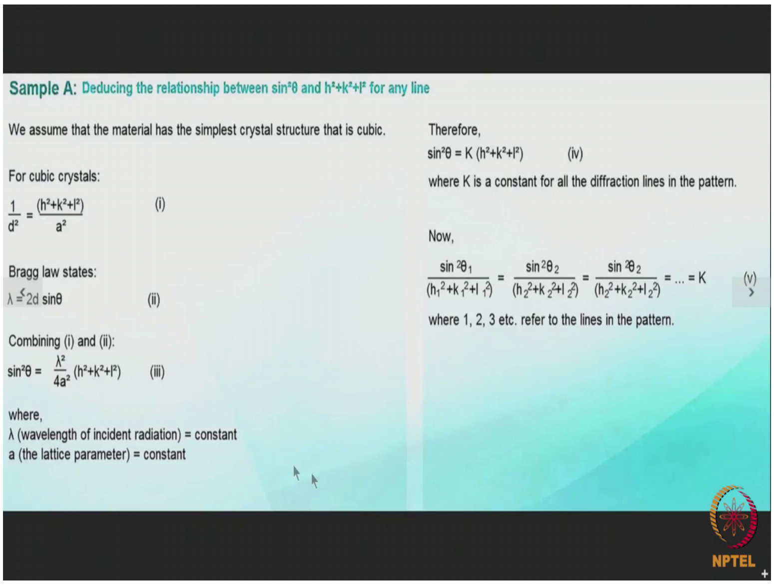

And the h k l values of that plane can be stated as 1 upon d square is equal to h square plus k square plus l square divided by a square where a is a lattice parameter of the material.

Now, we know that Bragg's law states the lambda is equal to 2 d sin theta. So, if we combine 1 and 2 by combining this 2 we can write sin square theta is equal to lambda square by 4 a square multiplied by h square plus k square plus l square where lambda is the wavelength of the incident radiation. So, Debye Scherrer method is a powder method. So, lambda is a constant value now is our lattice parameter of the material. So, that is also a constant value. So, in this equation here lambda square by 4 a square is a constant for all the lines in the pattern therefore, we can write sin square theta is equal to k times h square plus k square plus l square where k is a constant for all the diffraction lines in the pattern.

If that be the case we can write down for line number 1 or line pair 1 sin square theta 1 divided by h 1 square plus k 1 square plus l 1 square should be equal to sin square theta 2 for this line pair number 2 divided by h 2 square plus k 2 square plus l 2 square equal to sin square theta 3 divided by h 3 square plus k 3 square plus l 3 square is equal to k now here there is a mistake please read sin square theta 3 here and these are h 3 k 3 and l 3.

So, 1 2 and 3 etcetera refer 2 the lines in the pattern. So, we come to a very important conclusion that if we divide the sin square theta values of the different lines by their corresponding h square k square plus l square value then for every line that will yield the coefficient the coefficient k a constant.

Now, we say that h k l are all integers. So, h 1 square plus k 1 square plus l 1 square or h 2 square plus k 2 square plus l 2 square or h 3 square plus k 3 plus l 3 square these are all individually integers. So, the relationship states simply this that if we divide the sin square theta value of line number 1 by an integer it will be equal to sin square theta value of the second line divided by another integer and that will be equal to sin square theta value for hard line pair divided by still another integer etcetera, etcetera, equal to a constant value.

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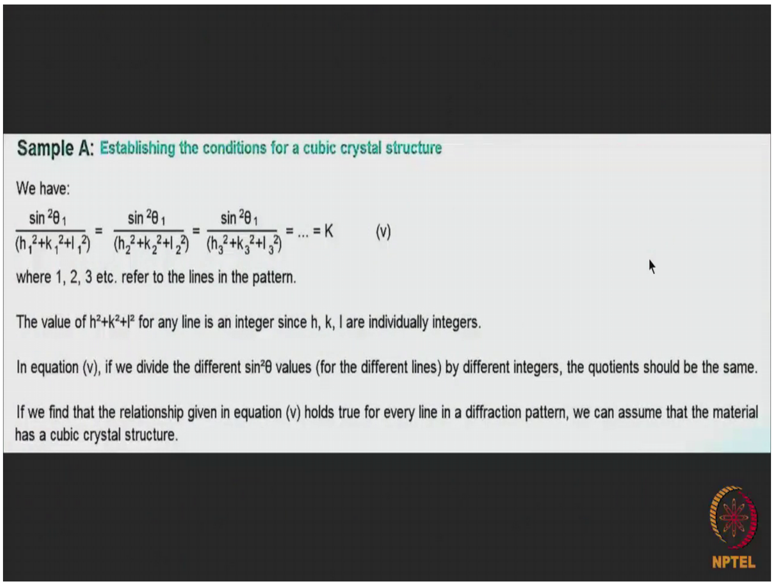

Now what are the values which h square plus k square plus l square can assume this is very important to know. So, we know that h square plus k square plus l square can assume only a certain values not every values now if suppose we find that this kind of a relationship is true for each and every line in the pattern then we can say that this pattern must be from a cubic material unless and until the material is cubic this kind of relationship will not be satisfied.

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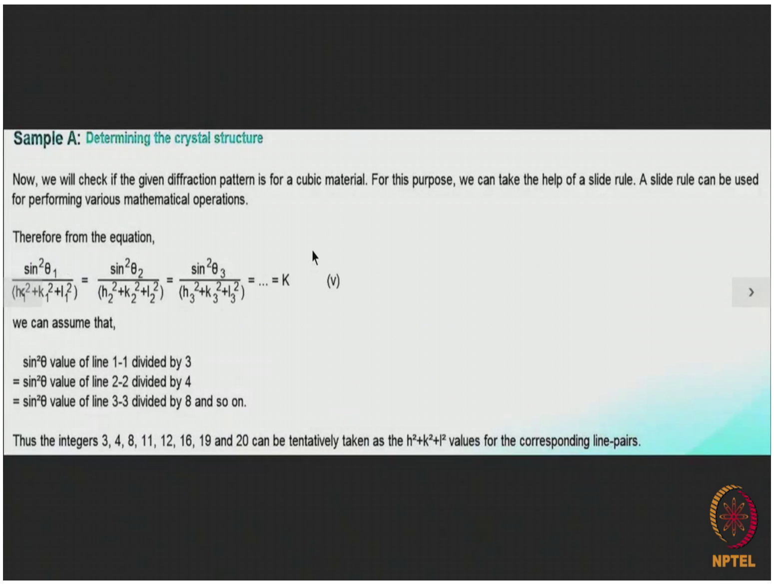

Say for example, if h k and l are such that h is 1 k is 0 l is 0 the what will happen if h is 1 k is 0 l is 0 then h square plus k square plus l square will be simply 1 if h is 1 k is 1 l is 0 then it will be 1 plus 1 2 if h is 1 k is 1 l is 1 then it will be 3 etcetera etc now in this particular case just you know if we divide the sin square theta value for line pair 1 1 by 3 then we shall see that this will be equal to the sin square theta value of the line pair 2 to divided by 4 and this will be equal to the sin square theta value of line pair 3 3 divided by 8 and so on.

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Table for Sample A

	2s	θ	$\sin\theta$	$\sin^2\theta$	$\frac{\sin^2\theta}{1}$	$\frac{\sin^2\theta}{2}$	$\frac{\sin^2\theta}{3}$	$\frac{\sin^2\theta}{4}$	$\frac{\sin^2\theta}{5}$	$\frac{\sin^2\theta}{6}$	$\frac{\sin^2\theta}{7}$
Line 1-1	6.46cm	22.03	0.375	0.141	0.141	0.070	0.047	0.035	0.028	0.023	-
Line 2-2	7.5cm	25.58	0.432	0.187	0.187	0.093	0.062	0.047	0.037	0.031	-
Line 3-3	10.97cm	37.41	0.608	0.370	0.370	0.185	0.123	0.093	0.074	0.062	-
Line 4-4	13.36cm	45.56	0.714	0.510	0.510	0.255	0.170	0.128	0.102	0.085	-
Line 5-5	12.28cm	48.13	0.745	0.555	0.555	0.278	0.185	0.139	0.111	0.093	-
Line 6-6	9.25cm	58.46	0.852	0.726	0.726	0.363	0.242	0.182	0.145	0.121	-
Line 7-7	6.40cm	68.18	0.928	0.861	0.861	0.431	0.287	0.215	0.172	0.144	-
Line 8-8	5.15cm	72.44	0.953	0.908	0.908	0.454	0.303	0.227	0.182	0.151	

Say for example, we prepare the following table. So, these are all the 8 lines we find on the pattern these are all the 2 S values for all the line pairs this is the value these are the value of theta sin square theta calculated from 2 S values and here we have got a chart sin square theta divided by 1 for all the 8 line pairs sin square theta divided by 2 for all the line pairs sin square divided by 4 for all the line pairs by 4 by 6 etcetera etc from this table we find that line 1 1 for the line 1 1 line pair 1 1 if it is sin square theta is divided by 3 it gives you a value of 0.047 again we find that sin square theta of line pair 2 2 when it is divided by 4 it gives a value of 0.047.

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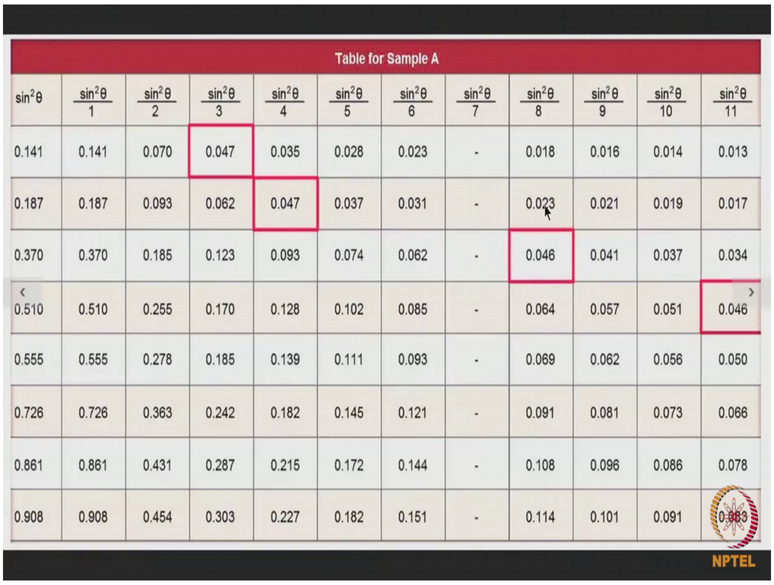

Table for Sample A

$\sin^2\theta$	$\frac{\sin^2\theta}{1}$	$\frac{\sin^2\theta}{2}$	$\frac{\sin^2\theta}{3}$	$\frac{\sin^2\theta}{4}$	$\frac{\sin^2\theta}{5}$	$\frac{\sin^2\theta}{6}$	$\frac{\sin^2\theta}{7}$	$\frac{\sin^2\theta}{8}$	$\frac{\sin^2\theta}{9}$	$\frac{\sin^2\theta}{10}$	$\frac{\sin^2\theta}{11}$
0.141	0.141	0.070	0.047	0.035	0.028	0.023	-	0.018	0.016	0.014	0.013
0.187	0.187	0.093	0.062	0.047	0.037	0.031	-	0.023	0.021	0.019	0.017
0.370	0.370	0.185	0.123	0.093	0.074	0.062	-	0.046	0.041	0.037	0.034
0.510	0.510	0.255	0.170	0.128	0.102	0.085	-	0.064	0.057	0.051	0.046
0.555	0.555	0.278	0.185	0.139	0.111	0.093	-	0.069	0.062	0.056	0.050
0.726	0.726	0.363	0.242	0.182	0.145	0.121	-	0.091	0.081	0.073	0.066
0.861	0.861	0.431	0.287	0.215	0.172	0.144	-	0.108	0.096	0.086	0.078
0.908	0.908	0.454	0.303	0.227	0.182	0.151	-	0.114	0.101	0.091	0.083

And when we divide the sin square theta value of line number 3 by 8 it gives us a similar kind of value 0.046 and if we go to the fourth line and divide it sin square theta by 11 it becomes 0.046. So, that indicates that for line pair 1 1 if we divide sin square theta by 3 that becomes equal to the sin square theta line pair 2 divided by 4 becomes equal to sin square theta value for line pair 3 divided by 8 that becomes equal to sin square theta of line number 4 divided by 11.

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Table for Sample A

$\frac{\sin^2\theta}{13}$	$\frac{\sin^2\theta}{14}$	$\frac{\sin^2\theta}{15}$	$\frac{\sin^2\theta}{16}$	$\frac{\sin^2\theta}{17}$	$\frac{\sin^2\theta}{18}$	$\frac{\sin^2\theta}{19}$	$\frac{\sin^2\theta}{20}$	hkl	a
								111	3.556
								200	3.556
								220	3.595
								113	3.595
								222	3.595
			0.045					400	3.635
						0.045		331	3.635
							0.045	420	3.635

So, it appears the pattern has been taken from a cubic material now in this way if we carry. In fact, we can find out that this is true for all the 8 lines in the pattern for example, you know the sin square theta of you know the sixth line when divided by 16 it also gives us same value as we had before then for this particular line seventh line sin square theta is divided by nineteen also gives us similar value 0.045 sin square theta by twenty from the eighth line gives us a value of 0.045 the same value.

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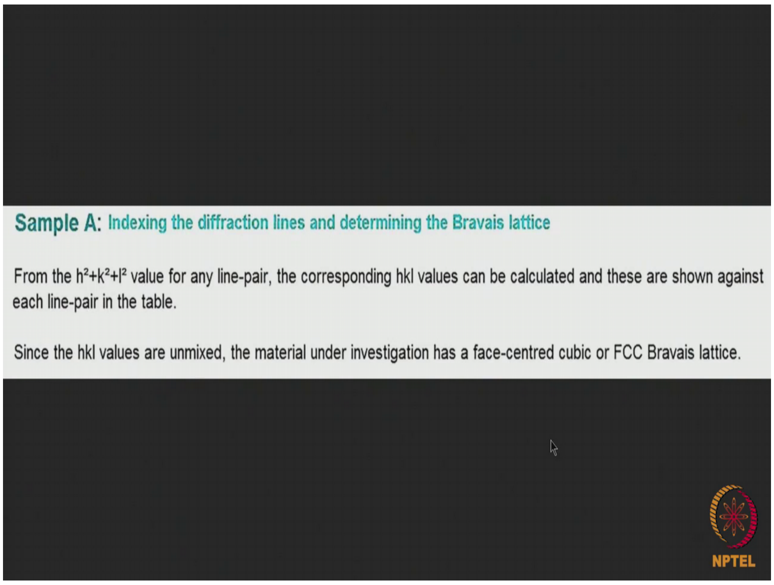

So, we say that for each and every line in the pattern if we divide the sin square theta of a particular line pair by an integer we find that you know the result is same for every one of the lines in the pattern.

So, if we know the value of the h square plus k square plus l square for any line pair we can easily write down what are the h k l values for those lines say for example, here for line number 1 these 3 is a value of the corresponding h square plus k square plus l square this is where the for line number 2 4 is the value of h square plus k square plus l square. So, if here h square plus k square plus l square is 3 and if a line 2 h square plus k square plus l square is 4 that indicates that in this particular case h k l will be 1 1 and 1 and what about this the h k l will be 2 0 0, similarly if we find for the third line 8 will be the corresponding h square plus k square plus l square for the line number 3. So, since it is 8 we can write h k l as 2 2 2 etcetera, etcetera.

So, in this way we can immediately write down the h k l values of the different lines say for line number 1 will be 1 1 1 line number 2 is 2 0 0 line number 3 2 2 0 line number 4 1 1 3 line number 5 2 2 2 6 4 0 0 line number 7 3 3 1 line number 10 a 8 4 2 0 etcetera etc. So, you see that initially we assume that the material is a simplest possible type it has got the cubic crystal system and we found out that the condition for a cubic crystal system has been fully satisfied by dividing the sin square theta values of the different line pairs by some integers which are nothing, but h square plus k square plus l square values for the different lines and since this relationship is fulfilled for each and every line of the pattern we can immediately say that the material is indeed a cubic material. So, crystal system is cubic.

Now, looking at the h k l values what we find the h k l values are such that they are all unmixed; that means, either all odd or all even say for example, here is all odd all even all even or all odd etcetera etc we know that when we have an face centred cubic material this is what happens the h k l planes which are unmixed; that means, either all odd or all even they will give raise to diffraction patterns. So, immediately we can come to the conclusion that the material has a cubic crystal structure not only that the brave lattice is FCC tie.

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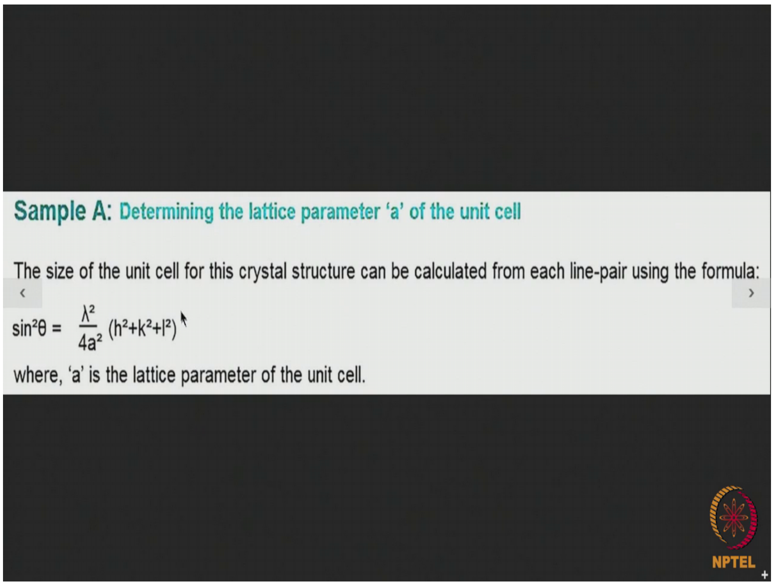

Now comes the third part of the problem; how to determine the lattice parameter of the unit cell? The material on the investigation now this can be done from this relationship which we found out earlier that for any line sin square theta is equal to lambda square by 4 S square into h square plus k square plus l square. So, we have now for every line found out the value of h square plus k square plus l square and the corresponding sin square theta value now lambda is known this is the wavelength of the incident radiation which is copper k alpha radiation in this case; that means, 1.542 angstrom. So, from this relationship the value of a can be easily determined.

And once we do that we can write down the value of; for calculated from each and every line so, this is the value of a for calculated from line number 1 this is the value of a calculated from line number 2 this is the value of a calculated from line number 2, this is the value of a calculated from line number 3, etcetera, etcetera. Now the question might be asked that a is a lattice parameter and it is a fixed quantity. So, how come we are getting all different values now we have to remember that whenever we do the calculations we make some manual measurements for example, 2 S values we determine manually.

Now this values when we measure there will always be some personal error and it is because of this that when we calculate the lattice parameter from the different lines the values to be different, but for some reason which I will explain later we take the lattice parameter determined from the highest angle line in the pattern to be the most accurate; that means, out of all these a values we have calculated far from the different lines we will consider this one calculated from the highest angle line in the pattern to be the most accurate.

We will find out the reason why very soon. So, we have found out for an unknown sample what is the crystal structure what is the brave lattice and what is the lattice parameter now let us take a second example here say this is a powder pattern obtained from the material using a Debye Scherrer camera and these are the different line positions on the film. Now as we have done in the previous method we calculate we determine our every measure the value of 2 S for each line pair and write them down now from this 2 S values we can find out the corresponding theta values the sin theta values and sin square theta values.

So, this is an unknown sample. So, how to start with first of all we assume that the material has the simplest crystal structure. So, we assume a cubic system for this unknown material.

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Table for Sample B

$\frac{\sin^2\theta}{1}$	$\frac{\sin^2\theta}{2}$	$\frac{\sin^2\theta}{3}$	$\frac{\sin^2\theta}{4}$	$\frac{\sin^2\theta}{5}$	$\frac{\sin^2\theta}{6}$	$\frac{\sin^2\theta}{7}$	$\frac{\sin^2\theta}{8}$	$\frac{\sin^2\theta}{9}$	$\frac{\sin^2\theta}{10}$
	0.062								
			0.060						
					0.059				
							0.060		
									0.060

And we know that it is quite easy to determine whether the material belongs to the cubic system or not say for example, we find in this case if the sin square theta value of line number 1 is divided by 2 is the same as the sin square theta value divided by 4 for the second line is the same as the sin square theta value divided by 6 in the from the third line is equal to sin square theta value divided by 8 for the 4th line is equal to sin square theta value divided by 10 for the sixth line for the fifth.

So, you see that you know all these are almost equal then that gives an indication that well like the previous case this material may also be belonging to the cubic system and in a manner which has already described for the previous pattern.

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Table for Sample B

$\frac{\sin^2\theta}{13}$	$\frac{\sin^2\theta}{14}$	$\frac{\sin^2\theta}{15}$	$\frac{\sin^2\theta}{16}$	$\frac{\sin^2\theta}{17}$	$\frac{\sin^2\theta}{18}$	$\frac{\sin^2\theta}{19}$	$\frac{\sin^2\theta}{20}$	hkl	a
								110	3.106
								200	3.153
								210	3.163
								220	3.147
								103	3.142
								222	3.030
	0.060							123	2.925
			0.059					400	2.851

We can immediately write down the corresponding h k l values from the h square plus k square plus l square values for each and every line and what we find here the h k l values are such that h plus k plus l is an even quantity. So, the h k l values of the lines are such that h k l equal to 0 in equal to an even number in each case and this is the condition for a body centred cubic structure if a material has a body centred cubic structure we know that h plus k plus l must be equal to an even number and this is what is true in this particular case. So, now, we have determined the crystal structure and brave lattice for this unknown material now we find out the value of a from the known relationship that exist between a and h k l as we did before and the values of a calculated in this manner are form to be.

So, you see that there is a wide variation in the value of a which is been calculated now as I told you before we take the value from the highest angle line as a most correct value of a. So, we consider this to be the most correct value of a let us now go to a third case say we have got a diffraction pattern for an unknown material here now the first step is to measure the 2 S values for each line pair as we did before say we when we do it there about thirty lines in the pattern and these are all the 2 S values.

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Table for Sample C

	2s	θ	sinθ	$sin^2θ$					
Line 1-1	5.25	18.06	0.310	0.096					
Line 2-2	5.56	19.13	0.328	0.108					
Line 3-3	6.22	21.40	0.365	0.133					
Line 4-4	7.7	26.49	0.446	0.199					
Line 5-5	10.1	34.74	0.570	0.325					
Line 6-6	11.2	38.53	0.623	0.388					
Line 7-7	13.6	43.22	0.685	0.469					
Line 8-8	10.44	54.09	0.81	0.656					
Line 9-9	9.4	57.66	0.845	0.714					
Line 10-10	8.24	61.65	0.88	0.774					
Line 11-11	7.68	63.58	0.896	0.803					
Line 12-12	7	65.92	0.913	0.834					
Line 13-13	6.1	69.02	0.934	0.872					

Now, if we deal with these values and assume that the material is a cubic material we know how to figure out whether the material is a cubic material or not. So, we apply the same criteria which we did before for the first 2 samples and if we do that we find that the lines in the pattern do not satisfy the requirement for a cubic material. So, we have to think again. So, it may be tetragonal in may be hexagonal it may be orthorhombic whatever. So, let us assume that this material has a hexagonal crystal structure.

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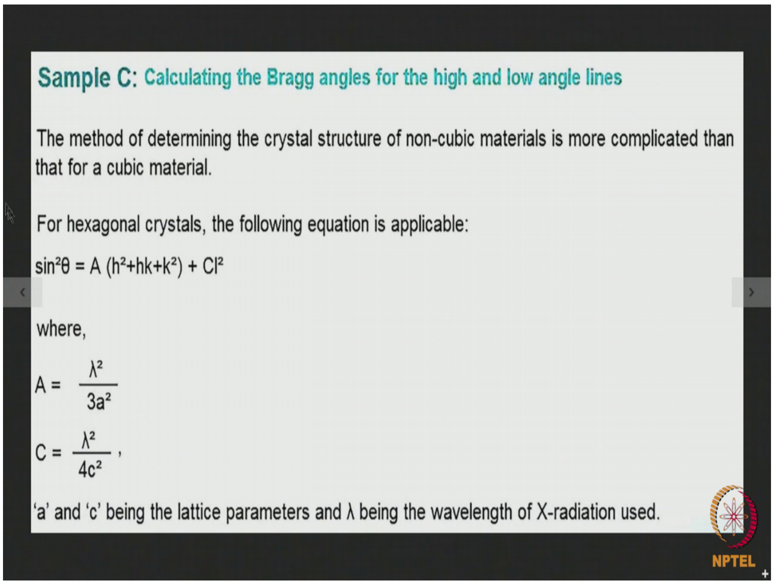

Now if we think about an hexagonal crystal structure then the relationship between sin square theta h k l and h k l are given by sin square theta is equal to a into h square plus h k plus k square plus c l square now we remember that in this particular case we have got 3 access of the same length A in 1 plane and axis perpendicular to the plane containing the 3 A axis. Now in this equation capital a stands for the lambda square divided by 3 a square and capital c stands for lambda square by 4 C square. So, A and small a and small c being the lattice parameters and lambda being the wavelength of the x radiation that we use.

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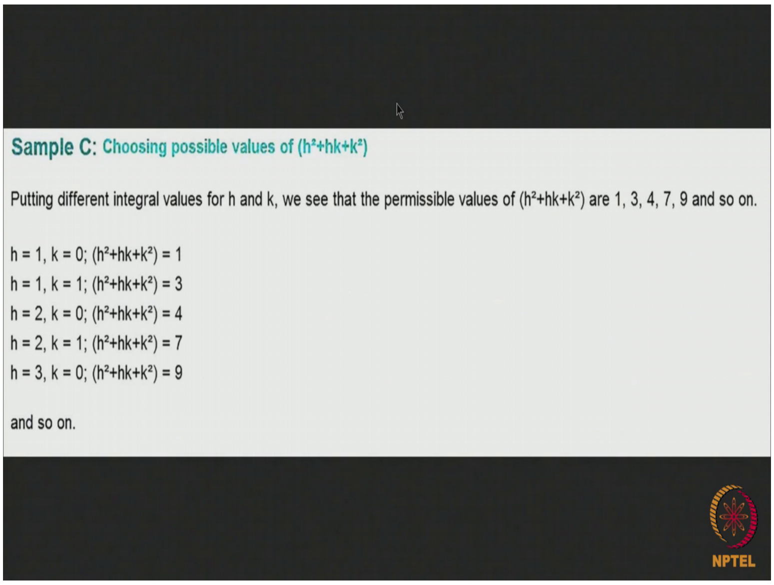

Now, as we did in the previous 2 cases from the 2 S values for each line pair we calculate the value of theta sin theta and sin theta and sin square theta in the usual manner now when we look at h square plus h k plus k square putting different values for h and k we find that h square plus h k plus k square can have the values 1 3 4 7 9 and so on in this case h is equal to 2 k is equal to 0. So, h square plus h k plus k square is equal to 1 then if h is equal to 1 k is equal to 1 then h square plus h k plus k square is equal to 3 etcetera, etcetera. So, these are the possible or permissible values of h square plus h k plus k square that will be 1 3 4 7 9 and so on.

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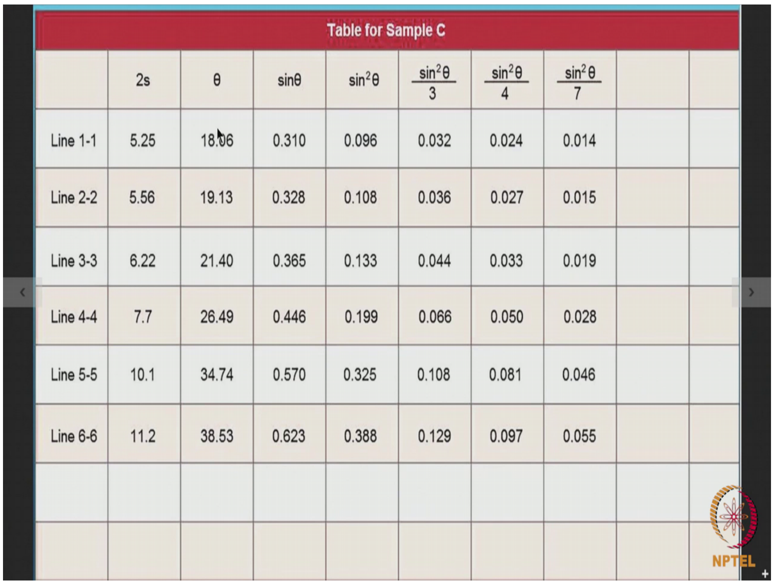

Table for Sample C

	2s	θ	sinθ	$sin^2θ$	$\frac{sin^2θ}{3}$	$\frac{sin^2θ}{4}$	$\frac{sin^2θ}{7}$		
Line 1-1	5.25	18.06	0.310	0.096	0.032	0.024	0.014		
Line 2-2	5.56	19.13	0.328	0.108	0.036	0.027	0.015		
Line 3-3	6.22	21.40	0.365	0.133	0.044	0.033	0.019		
Line 4-4	7.7	26.49	0.446	0.199	0.066	0.050	0.028		
Line 5-5	10.1	34.74	0.570	0.325	0.108	0.081	0.046		
Line 6-6	11.2	38.53	0.623	0.388	0.129	0.097	0.055		

To make life easier let us consider only the first 6 lines in the pattern line pair 1 1 line pair 2 2 line pair 3 3 4 4 5 5 and 6 6, these are the 2 S values these are the theta values these are the sin theta values these are the sin square theta values now what we do we divide the sin square theta values by 1 3 4 7 etcetera which are the permissible values for h square plus h k plus k square say for example.

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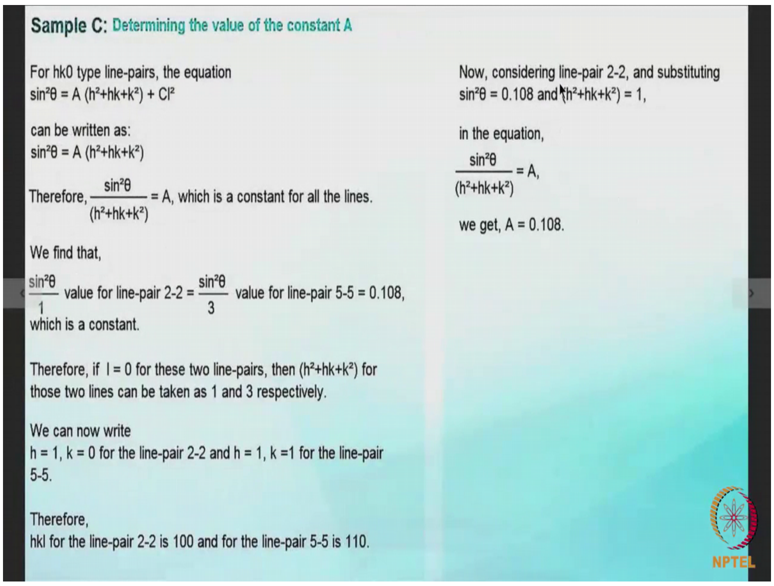

If there are some lines having the indices h k 0; that means, l is equal to 0. So, there may be some lines may or may not be there may be some lines for which the n is 0. So, these are h k 0 type line pairs. So, if we have got such lines in the pattern then the equation sin square theta is equal to a into h square plus h k plus k square is equal to c l square can be written simply as sin square theta is equal to a into h square h k plus k square for h k 0 type of lines if it is h k 0 type of lines l will be 0.

So, in that case this equation can be written in this form therefore, we can write from this equation sin square theta divided by h square plus h k plus k square must be equal to a which is a constant for all the lines now if we go back to the previous diagram here we will see that sin square theta by 1 for line pair 2 2 is equal to sin square theta value by 3 for line pair 5 5 and is equal to 0.108 as it is becoming quite clear.

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Table for Sample C

θ	sinθ	$\sin^2\theta$	$\frac{\sin^2\theta}{3}$	$\frac{\sin^2\theta}{4}$	$\frac{\sin^2\theta}{7}$	$\frac{\sin^2\theta}{A}$	$\frac{\sin^2\theta}{3A}$	hkl	
18.06	0.310	0.096	0.032	0.024	0.014				
19.13	0.328	0.108	0.036	0.027	0.015			100	
21.40	0.365	0.133	0.044	0.033	0.019				
26.49	0.446	0.199	0.066	0.050	0.028				
34.74	0.570	0.325	0.108	0.081	0.046			110	
38.53	0.623	0.388	0.129	0.097	0.055				

So, you see that for the line pair 2 2 the sin square theta by the; I am sorry sin square theta by 1 for line pair 2 2 becomes sin square 3 by 2 by 3 value for the line pair 5 5 and the value is 0.108. So, these are the values which we obtain.

So, what does that indicate it indicates that it could be that the line pair 2 2 and the line pair 5 5 could be h k 0 type lines. So, it appears this could be the h k 0 type lines therefore, if n is equal to 0 for this 2 line pairs then h square plus h k plus k square for these 2 lines can be taken as 1 and 3 respectively. So, once we do that we can immediately find out if the h square plus h k plus k square is 1; that means, the line will be 1 0 0 and for line pair 5 h square plus h k plus k square is equal to 3; that means, it will be the line 1 1 0 now if we go back to the previous diagram. So, we can see that the h k l for the line pair 2 2 can be tentatively written as 1 0 0 and the h k l value for the line pair 5 5 can be tentatively written as 1 1 0.

Now, if we consider the line pair 2 2 only and substitute the value of sin square theta which is 0.108 and h square plus h k plus k square is equal to 1 then from this equation we can find out the value of a constant which is 0.108.

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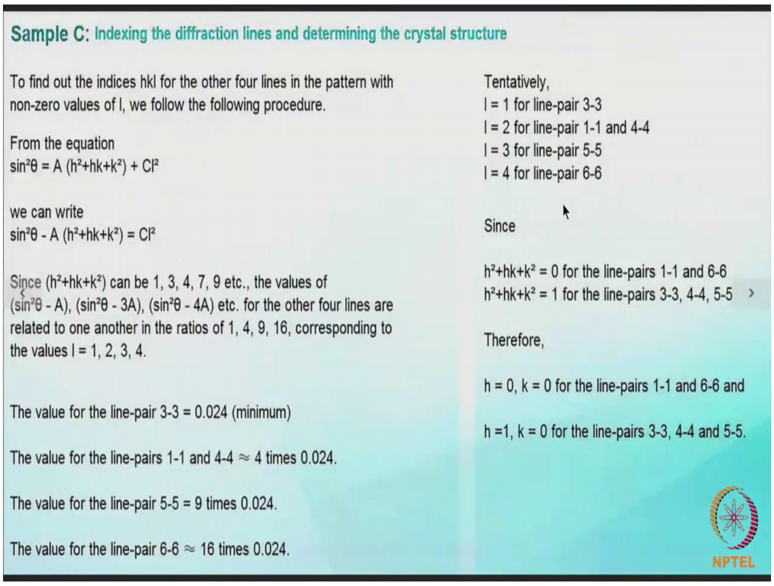

Now what about the indices h k l of the other 4 lines in the pattern which do not have 0 l value then we follow the following procedure say from the equation sin square theta is equal to a into h square plus h k plus k square C l square we can write it in this form sin square theta minus this term is equal to C l square now you have already know that h square plus h k plus k square can assume values of 1 3 4 7 9 etcetera.

So, if we subtract the values of a into 1 A into 3 A into 4 A into 7 A into 9 etcetera then these values for the other 4 lines should be related to 1 another in the ratio of 1 4 9 16 etcetera corresponding to the values of l is equal to 1 2 3 4. So, what I am repeating the case you see from the basic equation we can rewrite the terms in this fashion now we know that h square plus h k plus k square they can have values of 1 3 4 7 9 etcetera so, the other 4 lines if for the other 4 lines if we subtract A into 1 A into 3 A into 4 A into 7 A into 9 from the corresponding sin square theta values then the values. So, obtained should be the ratio of 1 4 9 16 etcetera because l can have can assume values of 1 2 3 4 etcetera.

Now, using this logic the value of the line pair 3 3 is 0.024 the values of the line pairs 1 1 and 4 4 are 4 times that the value for the line pair 5 5 is times that the for the line pair 6 6 is 16 times that now if you go to the next diagram, it will be quite apparent. So, you see that.

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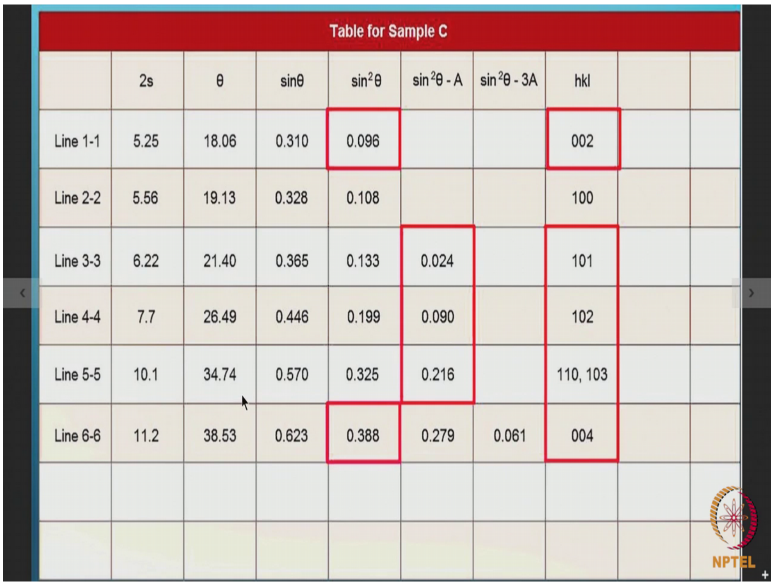

Table for Sample C

	2s	θ	sinθ	$sin^2θ$	$sin^2θ$ - A	$sin^2θ$ - 3A	hkl		
Line 1-1	5.25	18.06	0.310	0.096			002		
Line 2-2	5.56	19.13	0.328	0.108			100		
Line 3-3	6.22	21.40	0.365	0.133	0.024		101		
Line 4-4	7.7	26.49	0.446	0.199	0.090		102		
Line 5-5	10.1	34.74	0.570	0.325	0.216		110, 103		
Line 6-6	11.2	38.53	0.623	0.388	0.279	0.061	004		

We have already found out that if we take the line pair 3 3 as shown here if we do at the line pair you know 3 3 now this has got a value of sin square theta minus a into 1 because here we have plotted we are able to determine 2 S theta sin theta sin square theta then sin square theta minus a into 1 sin square theta minus 3 you know a into 3 etcetera, etcetera.

So, here we find that this value here for line pair 3 3 is 0.024 where as these value here which is sin square theta minus 0 into a is 0.0964 times this is also for line pair 4 this is also almost 4 times this value this is 9 times this value here and this is you know 16 times the value over here. So, tentatively if we can put l is equal to 1 in this case then these l will be 2 over here and 2 over here then it will be 3 over here and 4 over here; that means, if l is 1 2 3 4 then the corresponding values will be like this that one is you know you know if this is l is equal to 1 then this will be l is equal to 4 this is l is equal to 2. So, it will be 4 times that and it will be 9 times that. So, corresponding if this is l is equal to 1 this will be l is equal to 3 this is 16 times this value. So, if this is l is equal to 1 this will be l is equal to 4.

Now, if we do that we can immediately write down the l value for the line pair 1 1 as 2 l value for line pair 3 3 as 1 l value for line pair 4 4 as 2 l value for line pair 5 5 as 3 and l value for line pair 6 6 as 4 and what about the h k values since here you know h and k h square plus h k plus k square how much it will be this is sin theta this is sin square theta. So, sin square theta minus 0 into that; that means, h and k must be 0. So, we can write down 0 0 here as indices h and k here for example, we find how much will be the h square plus h k plus k square over here in this problem h square plus h k plus k square must be equal to 1.

So, for this h and k must be 1 and 0. So, we write down 1 and 0 what about this line this also comes under this column where h square plus h k plus k square is simply equal to 1; that means, h and k are 1 and 0. So, we write down h and k values as 1 and 0 what about this value here it also comes under this column. So, h and k must be 1 and 0s. So, we write 1 and 0 and what about this value it comes under this column where h and k are 0 and 0. So, we can write 0 0 and this we already determine earlier and this we have already determined earlier. So, we say that line number 5 can arise due to both planes 1 1 0 and 1 0 3 and they will appear at the same place because d is the same for both kinds of planes.

So, now we have found out the h k l values of all the planes which will give raise to diffraction in this particular case. So, we have been able to index all the lines by using the same logic.

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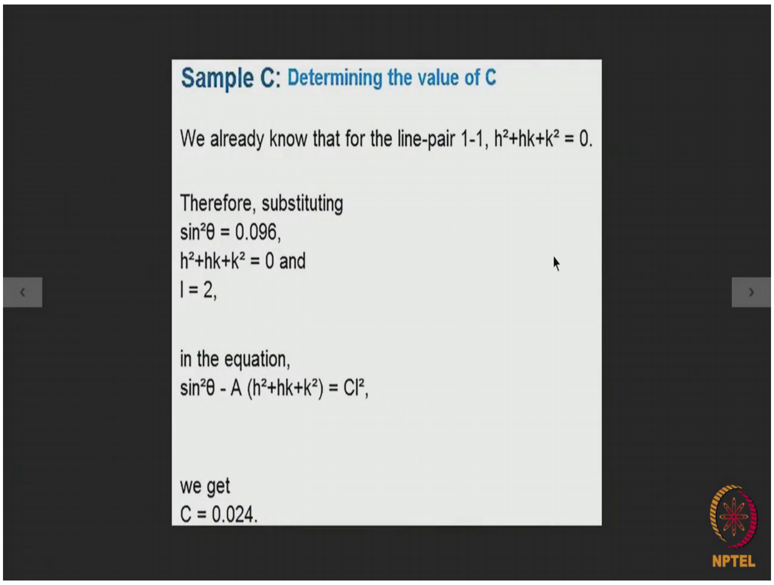

Now, we already know that for the line pair 1 1 h square plus h k plus k square is 0 therefore, when we substitute for sin square theta it will be 0.096 h square plus h k plus k square is equal to 0 and l is equal to 2 in the equation sin square theta and when you put this values in the equation sin square theta minus a into h square plus h k plus k square plus c l square we get c is equal to capital C is equal to 0.024. So, we have already calculated the value of the capital A and the capital c which are constants for all the lines in the pattern.

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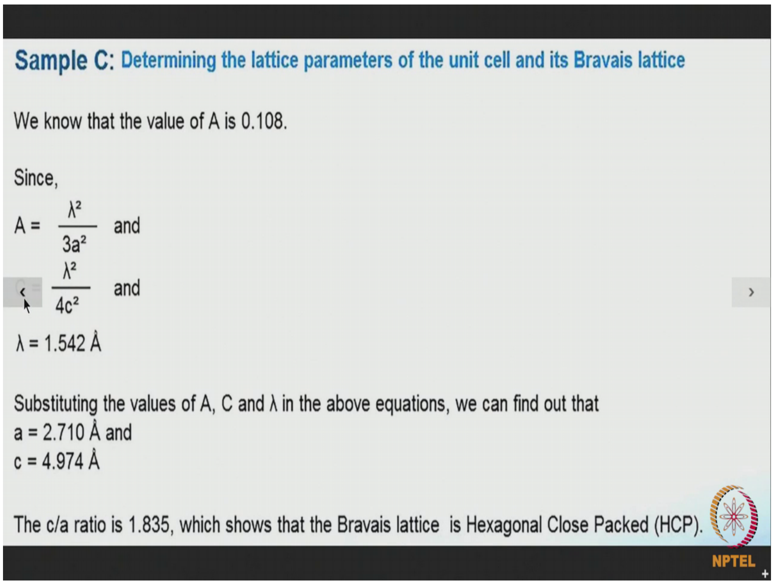

Since capital A is lambda square by 3 a square and capita C is equal to lambda square by 4 c square and the and the lambda the wavelength of the radiation we use was 1.542 angstrom substituting all those values in the above 2 equations we find a then one of the lattice parameters you know as 2.710 angstrom and the c is equal to 4.974 angstrom now the C by a ratio is 1.835 which shows that it is a hexagonal closed pack structure you see this is wrong to say that this is a Bravais lattice this is not a Bravais lattice. So, this material that we have examined is a material which has a hexagonal close pack structure.

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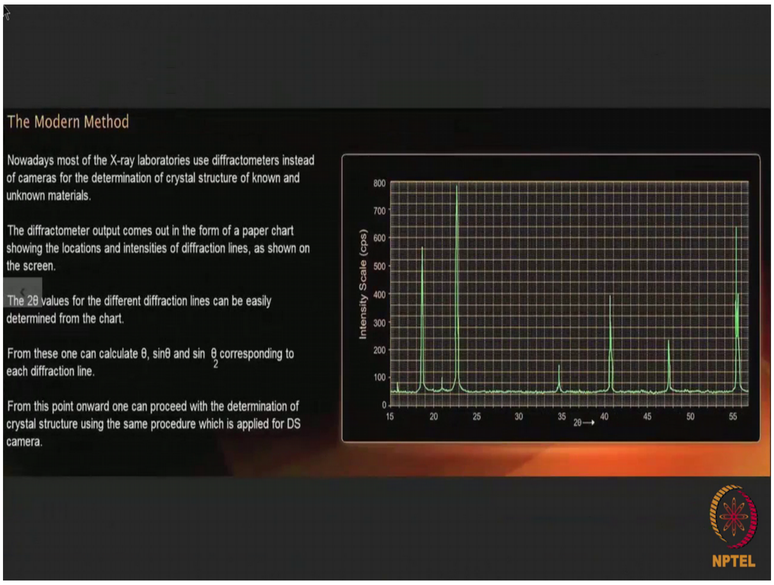

Now, we talk about the modern method you see nowadays we use the X-ray diffractometer in most of the labs instead of the cameras for the determination of crystal structure of known and unknown materials now diffractometer output comes out in the form of a paper chart showing the location and intensities of diffraction lines as shown on the screen. So, this is the intensity of a diffraction line and this is the 2 theta along x axis the 2 theta values for the different diffraction lines can be easily determined form the chart.

So, that you can figure out the exact 2 theta values for the different lines over here you know all these high intensities lines are similar to the lines which appear as lines on a photographic film in the Debye Scherrer camera. So, one advantage of the diffractometer meter method is you can accurately read out the value of theta for each and every line from the chart and once you determine the value of theta using the same method as before we can find out the value of sin theta and sin square theta and from there we can follow the same procedure as we did with respect to Debye Scherrer photographs.

So, in this way you know if you have got a diffractometer plot from that also we can easily figure out the values of theta for each and every line straight away and then from there we can measure sin theta we can determine the sin square theta and then deal with these numbers in the same way we did for the Debye Scherrer photographic you know method and determine the crystal structure.

Now, in the next chapter we shall be dealing with how to measure the lattice parameter or the lattice parameters very very precisely for example, we have already seen that depending on the calculation depending on the diffraction line from which the a values are determined there are different values of a or different values of c, but actually these are constant for the material and as I have already said that these arises due to error in the measurement of 2 S or error in the measurement of theta.

So, in the next chapter, I will deal with the technique or method of determining the lattice parameter or parameters very very precisely.