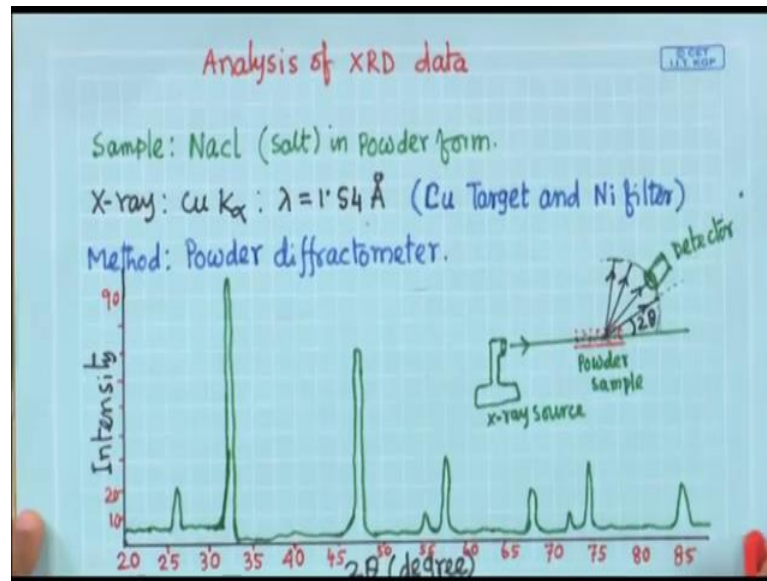


Experimental Physics - III
Prof. Amal Kumar Das
Department of Physics
Indian Institute of Technology, Kharagpur

Lecture - 62

Today I will discuss about the analysis of XRD data. I have shown you the instrument and that instrument is used to take the data from a sample.

(Refer Slide Time: 00:46)



This if you give sample to operator really they will do experiment for safety reason and they give you a set of data like this. Here sample is sodium chloride, salt whatever we eat salt that salt in powder form. Now, X ray is used for this experiment is copper K alpha it is wavelength is 1.54 angstrom.

Copper target and nickel filter is used to get this copper K alpha on the sample. this method is powder diffract diffractometer. Powder diffractometer geometry is like this. This is the X ray source X ray is coming and falling on powder sample. Now, this is the direction of incident X ray. Now, the diffracted X ray in different direction that direction is 2θ with respect to this incident direction.

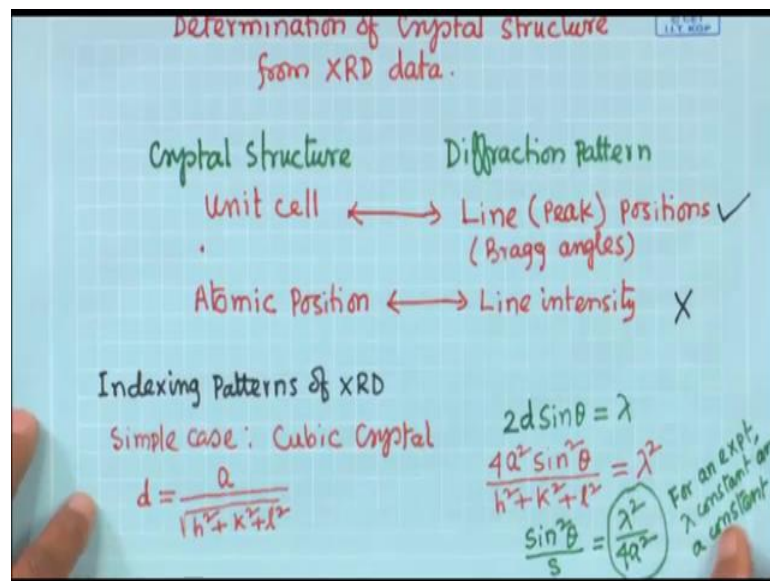
A detector it just move in a circle to record the diffraction data. if you plot these data. This data you will see in a plot like this. There are some peaks of different intensity and different peak width. From these data, what you are seeing? You are seeing there is

number of peaks is called Bragg peaks and the different peaks have different intensity and also they are not very sharp peaks, but there is a width this peak position in terms of angle, angle 2 theta.

Here you will be able to see angle 2 theta. that is the detector angle with respect to the incident direction of X ray. Generally, we plot intensity versus 2 theta. the position of the peaks in terms of angle, intensity of the peaks and width of the peaks all these three contain information about the sample.

We have to analyse the peak position in terms of; in terms of angle then peak intensity as well as peak width. These three will give us information about the; about the sample. What are the information we can get?

(Refer Slide Time: 04:46)



First very important information you would like to know that is crystal structure, whatever sample we have taken. What is the structure crystal structure of that sample that we would like to know?

This crystal structure in one hand and in other hand, we have diffraction pattern. Relation between these two is unit cell corresponds to line or peak position, this is Bragg angle and the atomic position in unit cell that corresponds to line intensity or peak intensity.

Here mainly I will discuss these peak position and peak width, but I will not discuss this intensity part because this slightly complicated and for higher study, we would like to

discuss this part, but this other part is not very difficult one. at this stage I would like to discuss only these line position or peak position and from there as well as peak width from there what are the information about the sample we can get. Here this actually we would like to we will be able to know about the crystal structure in terms of unit cell; what is the size of the unit cell, what is the lattice parameters, so that we will be able to find out.

That diffraction pattern I have shown you, so there are many peaks. First task is to index those peaks that is called indexing patterns of XRD. crystal structure there are 7 crystal system and 14 Bravais lattice. Out of 7, one system is cubic system; cubic crystal, so that is the simplest one.

I would like to take this example since this sodium chloride that data I have shown you that is that sodium chloride have cubic structure. I will discuss in terms of cubic structure, but for other structure also similarly one can; one can do the analyse the data.

see in case of simple, in case of cubic crystal see you know the relation between the lattice parameters and the and the planar spacing d . d equal to a by square root of $h^2 + k^2 + l^2$. h, k, l or miller indices. from here and this is from crystal part from crystal we know this relation. Now, this for XRD patterns. we that pattern we find we get, so that follows these $2d \sin \theta = \lambda$ equal to one we have taken for the first order we are considering.

If I put this d , value here and square on both side. you will get $4a^2 \sin^2 \theta$ divided by $h^2 + k^2 + l^2$ equal to λ^2 I can rearrange and I can write $\sin^2 \theta$ by S equal to λ^2 by $4a^2$. Now, you can see from this relation for an experiment we use a particular λ is constant and we use a particular sample. that sample that lattice constant a is also constant. This part, λ^2 by $4a^2$ is constant and that is equal to $\sin^2 \theta$ by S .

Now, θ is the Bragg angle of different peak; of different peak and S is sum of the square of the miller indices. From pattern, XRD pattern, there are many peaks we can tell this peak number 1, peak number 2, peak number 3 here, peak number 1, peak number 2, peak number 3, 4, 5 these are peak number. In addition, these peaks have these angle these 2θ from there we can find out θ . we can easily calculate $\sin^2 \theta$.

Now sin square theta divide by divide by S, S is this s is this one for different S there will be different h k l. what are the possible; what are the possible S? S can be; S can be is always integer S is always integer you can because h k l is integer.

(Refer Slide Time: 11:15)

$\frac{\lambda^2}{4a^2}$ is constant for all peaks. Find 2θ for different Bragg peak calculate $\sin^2\theta$

Peak no.	$S = h^2 + k^2 + l^2$	Cubic Simple	Face centered	Body centered	Diam
1	1	100	—	—	—
2	2	110	—	110	—
3	3	111	111	—	111
4	4	200	200	200	—
5	5	210	—	—	—
6	6	211	—	211	—
7	—	—	—	—	—
8	8	220	220	220	220

S will be integer means; h square plus k square plus l square is always integer and lambda square by 4 a square is constant for all peaks. for all peaks these will be constant. sin square theta by S, sin square theta experimentally we are getting from the peak position. this S; this S sin square theta we will calculate for different peak for different peak and this you can write S equal to h square plus k square plus l square. it can be 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, just you write upto say 20, here I have written up to 8.

Now, for 1; only one combination 100, this h k l this value is only possible. This is it is 1 it is 100 family. It is not only 100 plane, it is the 010, 001 all sorts of planes under this. this it is not one plane, but it is a family of planes. That we tell we write in second bracket. 100, for 2; only h, k, l value can be 110, again it is a not one plane it is the plane of family of some planes like 110, 101, then 011

For 3; 111, for 4; 2 0 0. No other combination is possible, 5; 2 1 0, 6; 2 1 1, 7; there is no possibility to have any combination of h k l. 8; 220 9 you can got 3 0 0. One can ahead not only 300 other combination maybe possible, so that that one has to see. now, you S is in your hand. Now, sin square theta also you we have got from the peak position.

those $\sin^2 \theta$ by S , by 1 by 2 by 3 by 4, just if you make a table then you will see that it again as I mentioned that this has to be constant, this has to be constant you will get a value you will get a value. That value for all peaks that that will remain constant that will be same value.

Now from that value one can find out; find out the; find out the a value lattice parameter that is a value one can find out in case of simple cubic. In cubic, there are 4 category; one is simple cubic, another is face centered cubic, then body centered cubic, another diamond also this in the cubic system.

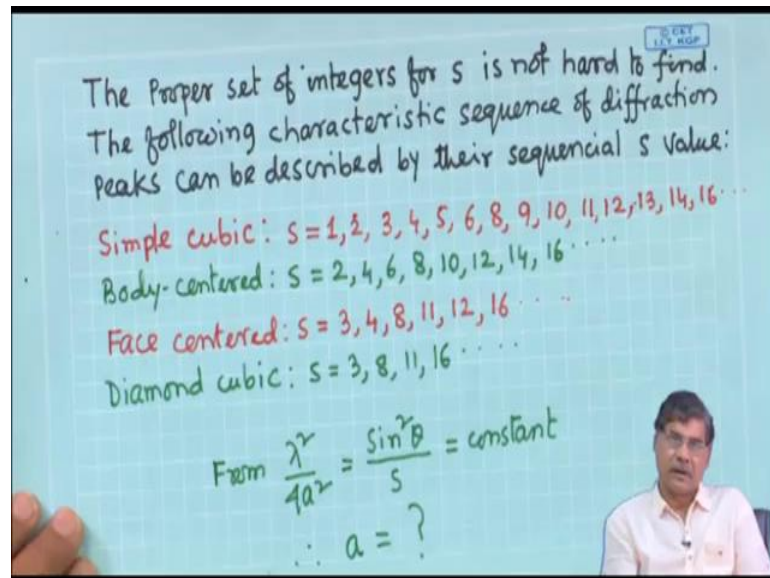
It is not the Bravais lattice diamond is not the Bravais lattice. Bravais lattice is this these three, but diamond it is FCC structure with additional lattice point additional more pore lattice point in the in the face centered cubic. You know that in simple cubic the number of lattice point per unit cell it is the 1 face centered cubic, it is a 4 body centered cubic, it is the 2 and diamond in case of diamond it is 8

This here I have written that for in case of simple cubic. these generally this all sorts of planes, all sorts of planes are these not all sorts of plane. Diffraction can be obtained from all planes, but when it is FCC, Face Centered Cubic. diffraction from all planes does not arise. Only these 111, 200 then, 220 then, other peaks arrive arise. in case of body centered cubics 110, 200, 211, 220. How you will find out? However, you will find out when $\sin^2 \theta$ from the pattern you will get and divide by this 1, 2, 3 4, 5.

then you will find that only for these for these peaks you are getting constant value, you are getting same value for other S , you are you are getting different value so; that means, that peaks are not there.

These peaks are absent. that way you will be able to identify that in case of simple cubic all sorts of planes or there for face centered cubic and body centered cubic and diamond these peaks will be available. from that itself you can identify their is in cubic whether it is face centered, whether it is body centered or it is diamond structure or simple cubic

(Refer Slide Time: 18:33)



What we saw that these the proper set of; proper set of integers for S is not hard to find the following characteristic sequence of diffraction peaks can be described by their sequential S value whatever in table I showed. These in case of simple cubic S value.

here it is there whatever x that pattern we have seen, so these peak number 1, 2, 3, 4, 5 if you just give a number and then those peaks will those peaks will satisfy the with this S value if it is simple cubic first peak. S is equal to 1, second peak 2, S equal to 2 third peak S equal to 3 that way for all sorts of S value, it will satisfy only missing is 7 and then 15 because this for these numbers you cannot get any you cannot get any set of $h k l$ value to yeah to for that S value

S value is $h^2 + k^2 + l^2$. Now, in case of body centered; first peak for that S equal to 2, for second peak S equal to 4 for third peak. all even number body centered cubic in that case S value is even number Now, face centered cubic that S value for first peak it will be 3 and then 4, 8, 11 like this.

In case of diamond, S value will be for first peak 3, 8, 11, 16. This sequence is written from you see this there are details reason for that it is a scattering atomic scattering from crystal

This intensity of the of the Bragg peak it depends on the structure factor and in structure factor atomic positions are included. From all planes, these diffractions are not allowed

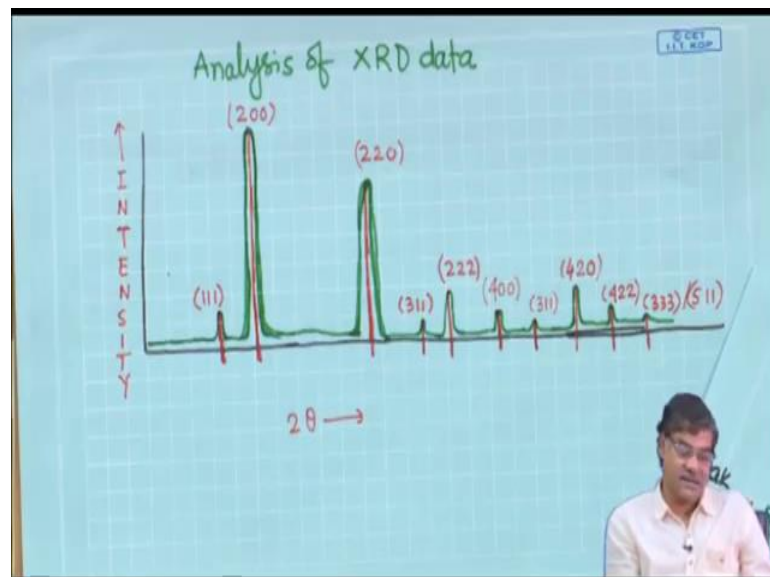
for only this S value the one can; one can get diffraction for these simple cubic or body centered or face centered or diamond cubic

This when you will get data from the lab, so they are giving you; they are giving you the raw data, you have to plot intensity over 2θ then you will see these different peaks at different angle. first task is to identify the angle or calculate the angle Bragg angle and from there you calculate $\sin^2 \theta$ and then you divide the $\sin^2 \theta$ by 1, 2, 3, 4, 5, 6, not 7, 8, 9, 10 then you find out these huge values are huge values are this constant $\sin^2 \theta$ by S huge value are same.

Those S values are for those peaks whatever you are seeing and if you see that S value is 1, 2, 3, all sorts of value. then it is simple cubic if it is only even value 2, 4, 6, then it is body centered if it is 3, 4, 8, 11, 12 then it is face centered and if it is 3, 8, 1, 11, 16, then it is diamond cubic this the analyses of the pattern, XRD pattern you have observed. Now, this whatever this $\sin^2 \theta$ by a S, so whatever the same for all peaks.

That value you know; that value you know, now λ value you know. you can calculate a value for simple cubic. This whatever this data I showed you initially these here. this there is no indexing of these peaks is the sodium chloride sample.

(Refer Slide Time: 24:25)



Now, whatever the way I told you from following that procedure you can just identify indexing the peaks indexing the peaks this is the peaks of sodium chloride Bragg peaks

from sodium chloride ok, here you can see these just for curiosity you can see that what are these sodium chloride is the FCC face centered cubic.

Here whatever for face centered cubic whatever I showed you that I think yes I showed you this for face centered cubic. peaks are 111, 200, 222 these are the peaks only you will see and this after that other peaks. Exactly here you can see 111, 200 then, 220 this is the third peak then fourth peak will be 311. 311 means 9, 11, 12. This for $12 S$ equal to 12 after yes.

For face centered what I told you that S equal to 3, S equal to 3 means; 111 then, I showed you this S equal to 4 means; 200 second peak, then third peak for face centered cubic 8 that is 2 2 0, then next value is 11

Next fourth peak is 3 1 1, 9 plus 1 10 plus 1 1 square of course, this 11. Then, this one is 12 1, 222 next is this 12. Next peak is 16; next peak is 16; 400 when from $\sin^2 \theta$ by S ; by S you are you are getting all these value constant all these value same.

Then from there from that S itself you can tell what is the; what is the plane it is the one 1 1 plane. This peak is from one one plane this peak is from 200 plane this way one can identify; one can identify the peak and one can tell what the structure is.

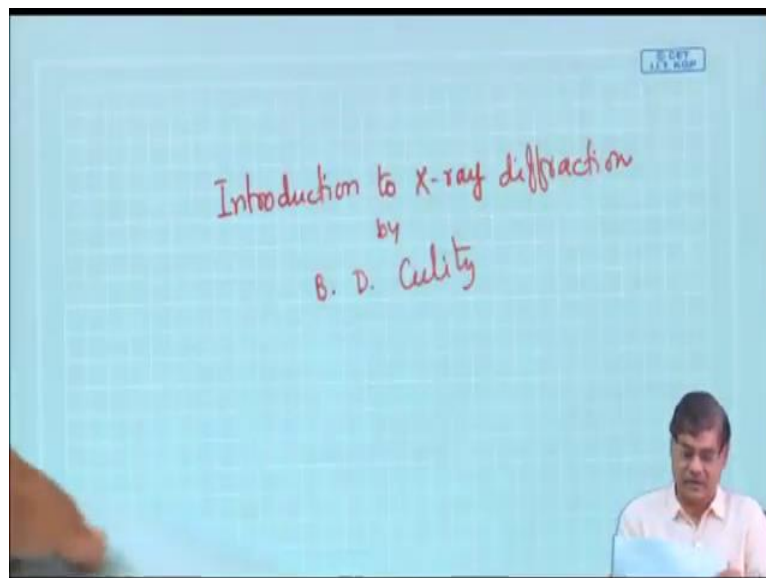
I discuss just taking example of; taking example of simple crystal; simple crystal. because this is the easiest one, but for other one also you can do for that you have to for simple cubic that is relation was d equal to a by square root of $h^2 + k^2 + l^2$. For other structure you have to know all this information here I have listed in any solid state physics book you will get. I followed whatever I am showing here.

(Refer Slide Time: 27:52)

Planar spacing for seven crystal systems

1. Cubic $\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$; $\cos\phi = \frac{h_1h_2 + k_1k_2 + l_1l_2}{\sqrt{(h_1^2 + k_1^2 + l_1^2)}\sqrt{(h_2^2 + k_2^2 + l_2^2)}}$
 $\hookrightarrow V = a^3$
2. Tetragonal $\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$; $\cos\phi = \frac{(h_1h_2 + k_1k_2)/a^2 + (l_1l_2)/c^2}{\sqrt{(h_1^2 + k_1^2)/a^2 + (l_1^2)/c^2}\sqrt{(h_2^2 + k_2^2)/a^2 + (l_2^2)/c^2}}$
 $\hookrightarrow V = a^2c$
3. Orthorhombic $\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$; $\cos\phi = \frac{h_1h_2/a^2 + k_1k_2/b^2 + l_1l_2/c^2}{\sqrt{(h_1^2/a^2 + k_1^2/b^2 + l_1^2/c^2)}\sqrt{(h_2^2/a^2 + k_2^2/b^2 + l_2^2/c^2)}}$
 $\hookrightarrow V = abc$
4. Trigonal/Rhombohedral $\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2)\sin^2\alpha + 2(hk + kh)\cos\alpha}{a^2(1 - 3\cos^2\alpha + 2\cos^3\alpha)}$; $\cos\phi = \frac{a^2d_1d_2}{a^2d_1^2 + a^2d_2^2 + (a^2d_1d_2)(\cos\alpha - \cos\alpha)}$
 $\hookrightarrow V = a^3(1 - 3\cos^2\alpha + 2\cos^3\alpha)$
5. Hexagonal $\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2}\right)$; $\cos\phi = \frac{h_1h_2 + k_1k_2 + l_1l_2 + (h_1k_2 + k_1h_2)\cos\alpha}{\sqrt{(h_1^2 + k_1^2 + h_1k_1)\frac{4}{3} + l_1^2}\sqrt{(h_2^2 + k_2^2 + h_2k_2)\frac{4}{3} + l_2^2}}$
 $\hookrightarrow V = \frac{\sqrt{3}a^2c}{2}$
6. Monoclinic $\frac{1}{d^2} = \frac{h^2}{\sin^2\beta a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} - \frac{2hkl\cos\beta}{ac}$

(Refer Slide Time: 28:23)



all these things I have noted down from the book that introduction I think I will write the name of the book that is Introduction to X ray diffraction, Introduction to X ray diffraction, I will write introduction to X ray diffraction; X ray diffraction by B D Culity ok

This is very famous book for X ray diffraction the experimental aspect of X ray diffraction. It is a nice book from that book only I have noted down all these all these information.

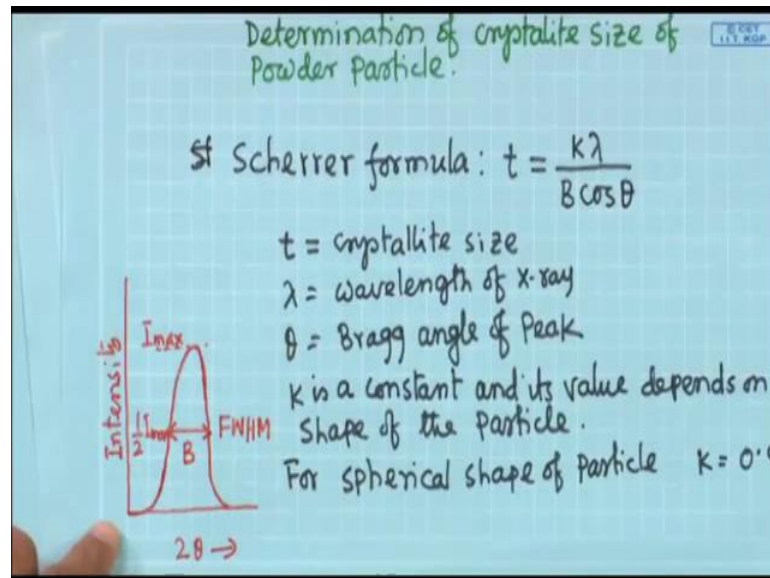
For cubic structure $\frac{1}{d^2}$ equal to $\frac{h^2}{a^2} + \frac{k^2}{a^2} + \frac{l^2}{a^2}$. For tetragonal, what is the relation orthorhombic what is the relation ok, what is the angle between these two plane $h_1, k_1, l_1, h_2, k_2, l_2$ in case of simple cubic in case of cubic structure we do not need α, β, γ because that we know this is the 90 degree ok, but in case of others other structure say triclinic or monoclinic say angles are different.

Here all relation you can see this is a, b, c and h, k, l value from XRD pattern, you passed you are indexing. When you are indexing; that means, you know the; you know the h, k, l value of this of the planes corresponds to that Bragg peak ok, h, k, l value is known to you for different peaks and then λ is known to you and then you can find out d value also you can find out from these $\sin^2 \theta$ value $\sin^2 \theta = \frac{\lambda^2}{d^2}$ then from there you are indexing h, k, l and then from this for that you are taking help of $S = \frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$

In case of simple cubic it is a simple, not simple cubic in case of cubic; it is that calculation is simple, but for other system, it is same way one has to proceed it is. You need not only a , you need a, b, c from one peak you cannot from one relation you cannot find out this value. you need more relation.

you need to analyse more number of peaks from this relation whatever I showed you here; I showed you here from this relation and the procedure I told you how to indexing the Bragg peak using this knowledge one can find out the determine the structure of the crystal

(Refer Slide Time: 32:19)



Then I told you that I will not discuss about the intensity of the peak, but I will discuss about. so far I discussed the position of the peak from there this you know you can find out the unit cell of the crystal and what are the lattice parameters ah.

Now, this width of the peak also very informative. From the width of the peak, one can find out the crystallite size of powder particle whatever the sample we have used this powder form. there are millions and millions particles are there. What is the size of those particles? Crystallite size, not physical size. One can find out there is a formula, readymade formula to find out the crystallite size. this is called a Scherrer formula Debye Scherrer formula; that is t the size of the crystallite size t equal to $K \lambda$ by $B \cos \theta$.

t is the crystallite size, again crystallite size and the physical size of the particle are not same generally crystallite size is less than the particle size. Here from XRD X ray diffraction we can find out crystallite size.

That maybe equal to the size of the particle or it may be less than that it cannot be greater than that λ is the wavelength, θ is the Bragg angle of peak. you take just one peak of higher intensity. For that peak what is the θ that for from the diffraction pattern XRD pattern you can find out θ . In addition, K is here this not K , it is not Boltzmann constant, it is a K is a constant and its value depends on the; its value depends on the shape of the particle.

Generally this for spherical shape of particle this K value is taken is 0.9. sometimes K people take just k equal to 1, but it is not exact. Theoretically people suggest for different value for spherical value this K is taken as 0.9 B is known lambda is known to us theta also we can get from the peak. Now what is B?

Just you from your XRD pattern you peak of a one peak and magnified if just plot in a in a magnified weak magnification now this B is B is full width at half maxima. full width at half maxima.

What is that? This peak what is the intensity of this peak? This I max intensity maximum at this peak. Now, half of the maximum intensity at this position, what is the width? What is the width? In radian, what is the width in radian it is the angle; what is the width in radian that is B from Bragg peak itself you can find out this is just B and theta peak position theta not 2 theta from here you will get 2 theta from that you have to find out theta. you can use this relation.

theta means, $\cos \theta$ you know, lambda you know, K values for spherical shape it is a 0.9 and then from the width of the peak you can this that is B and you can calculate the size of the particle, it is not size of the particle size of the crystal of the crystal or crystallite size, we tell generally.

This way from peak position from peak width, we can get the crystal about the crystal structure, we can get the information about the particle size and peak intensity we can get lot of information. there are this a very vast subject there are many more things, but I think that is a basic things I discuss here. That is enough for this stage.

I think this if you should practice using different XRD patterns even from the say internet and try to find out just how to identify the peaks and their corresponding h k l value and how to find out the lattice constant, how to find out these particular size I think I will stop here.

Thank you for your attention.