X-Ray Crystallography

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Lecture - 30
Tutorial 07
Precise Lattice Parameter Determination 1

Hello everyone. Welcome to this X-ray Crystallography course. I would like to take some problems on crystal structure determination in this tutorial class. I hope all of you must have seen in the lecture that couples of examples have been solved, how to determine the crystals structure, and also how to find out the lattice parameter. In fact, you can find the lattice parameter through these X-ray diffraction techniques, 2 ways.

One is a normal, I mean lattice parameters you which you derive it from the Bragg's law. And also you can also find out this lattice parameter much more precisely, which has been demonstrated in the lecture notes. I will also solve one problem related to this precise lattice parameter determination. And before I even start this problem I would like to review the basic concepts involved in this crystal structure determination. What I will do is I will take a simple cubic systems, which is much more easy to solve compare to the other I mean, the X-ray data pertaining to other crystal system which are bit complex.

So, we will lay out some simple procedures to solve the; I mean, identify the crystal structure for a cubic system. Then I will go through the precise lattice parameter determination and so on. So, I will solve 3 problems. And before I even solve the problems I would like to review the basic concepts underlying the crystal structure determination using X-ray data.

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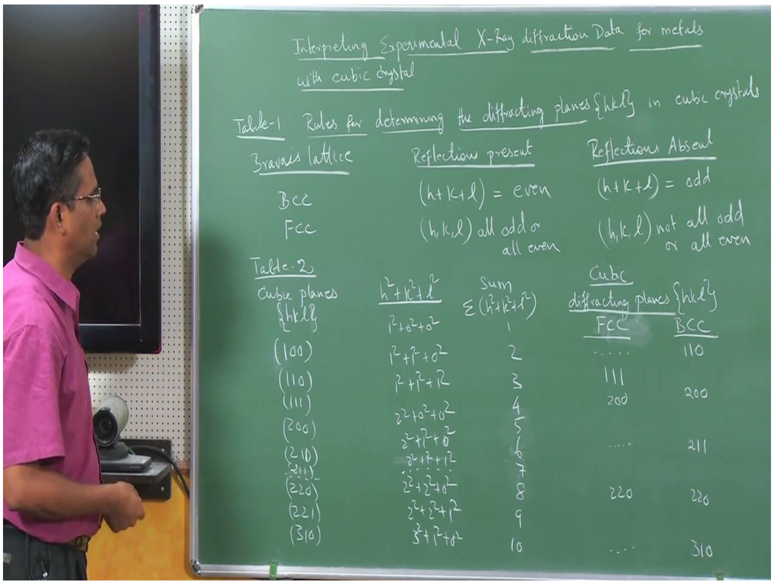

We have just reviewed the rules for determining the diffracting planes in a cubic crystal. So, we take it up the body centered cubic lattice as well as the face centered cubic lattice.

And if you look at what kind of reflection will be present in the X-ray data is h plus k plus l is equal to even. And h plus k plus l is equal to odd. This will be absent and this will be present. And if it is going to be in FCC it is h k l all odd or all even. And what is going absent h k l not all odd or all even. So, based on this selection rules if you look at the cubic planes h k l, you start from 1 0 0 all the way up to 3 1 0. If you compute this h square plus k square plus l square, and then sum it up like this, and then you see that the corresponding diffracting plane according to the above table.

For an FCC you see that 1 1 1, 2 0 0 and 2 2 0 so; that means, either it is all odd or all even. So, that kind of selection rule, here for an FCC and for a BCC it is h plus k plus l is equal to odd or odd will be absent even will be present. So, to 1 plus 1 is equal to 2, even number 2 is even number 2 plus 1 plus 1 is equal to 4, even number 4 and again 4. So, all this reflection reflecting plane will be present in the case of BCC. So, this is well known you must have already clear about this aspect.

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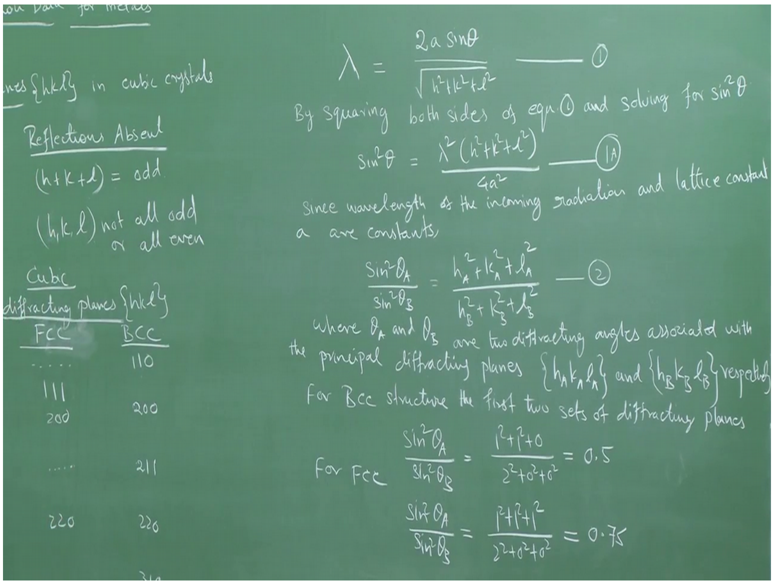

So, what is the basic relationship one can derive from the X-ray diffraction rules is something like you have So, from the bragg law as well as the relationship between the lattice parameter and the inter planar distance d one can derive this equation. N lambda is equal to 2 d sin theta as well as d is equal to a by square root of it is square plus a k square plus l square. From there you can find out this relation and what is the usefulness of this relation, suppose if we by squaring this.

So, what I have done is from this relation, we can by squaring this equation both sides and then if you solving for sin square theta you get this expression right. So, let us name it as 1 a, and then since the wavelength of incoming radiation and the lattice constants or constant values, you can rewrite this equation like this. Sin square theta A by sin square theta B is equal to h A square plus k A k A square plus l A square, by h p square plus k B square and plus l B square. Where theta A and theta B are the 2 diffracting angles associated with principal diffracting planes h A k A l A and h B k B l B respectively.

So, this is very useful relation, because you have the table here, where it clearly given the diffracting, principal diffracting planes pertaining to FCC and BCC, and then if you can take the first 2 sets of diffracting plane from the table for a BCC, and then solve this you get about and you substitute this into this equation and then see, the value is about 0.5. Similarly for FCC if you take the first 2 principal diffracting planes and then if you substitute those values into this equation and you get about 0.75. This is an useful relation; so if you have the first 2 reflection planes and if you find the ratios of this, and if you get 0.5 and 0.75.

So, from an unknown crystal structure, cubic crystal unknown cubic crystal it could be a simple cubic or it could be BCC or in FCC. And this is one shortcut to find out the correct crystal system.

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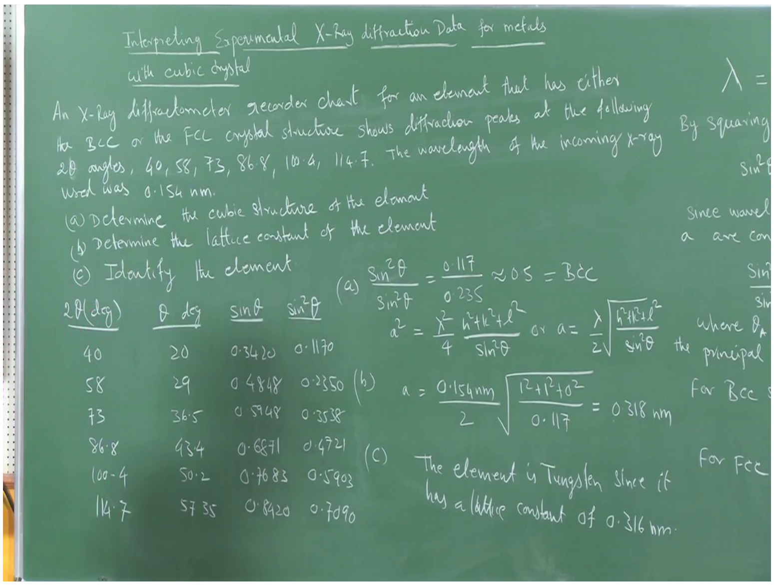

So, what I will do is to illustrate this, I will take up one problem, and then I will move on to the next. So, the problem here is, an X-ray diffractometer recorder chart for an element that has either the BCC or the FCC crystal structure, shows diffraction peaks at the following 2 theta angles.

40, 58, 73, 86.8 100.4, 1, 1, 114.7 the wavelength of incoming X-ray used was 0.154 nanometer. Determine the cubic structure of the element determine the lattice constant of the element identify the element. So, this is the question. So, we have to find out whether these 2 theta value gives any of this whether it follows any of this trend. So, first what we have to do? First we have to find out we have the 2 theta angle value. So, let us look at the sin square theta. So, we have 2 theta degrees.

So, then we will convert that into theta, then sin theta then sin square theta. We have this sin square theta values. We are considering the first 2 set of value. So, we will take 0.117 divided by 0.235 which is approximately close to 0.5. So, according to this, this is crystal structure is BCC. So, for determining the lattice constant again, we know that this relation.

So, you we have what we have done here is, again we have substituted the values of h k l in this formula and the answer is 0.318 nanometer. And if you can compare in the literature, the element tungsten has got the lattice constant of 0.316. So, the answer is tungsten and it is BCC. So, what we have demonstrated through this problem is, ratio of sin square theta value is quite useful in determining the crystal structure, and as well as the lattice constant of the given X-ray diffraction data. So, what I will do now is we will just go through couple of more problems.

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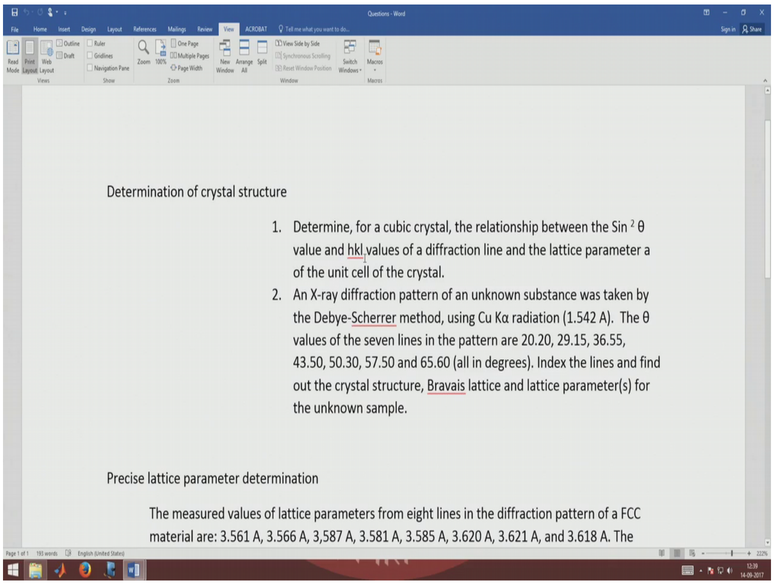

Which I am going to project it down the screen, if you look at this screen determine, for a cubic crystal the relationship between sin square theta value and h k l values of a diffraction line and the lattice parameter of the unit cell of the crystal. Which is nothing but this is the relationship, what we have shown that is the part of that is the answer for this question. And X-ray diffraction pattern of an unknown substance was taken by the Debye scherrer method.

Using a copper k A radiation that is 1.542 angstrom. The theta values of this 7 lines in the pattern are 20.20, 29.15, 36.55, 43.5 50.3, 57.5 and 65.6, all in degrees index the lines and find out the crystal structure; Bravais lattice and lattice parameter for the unknown sample.

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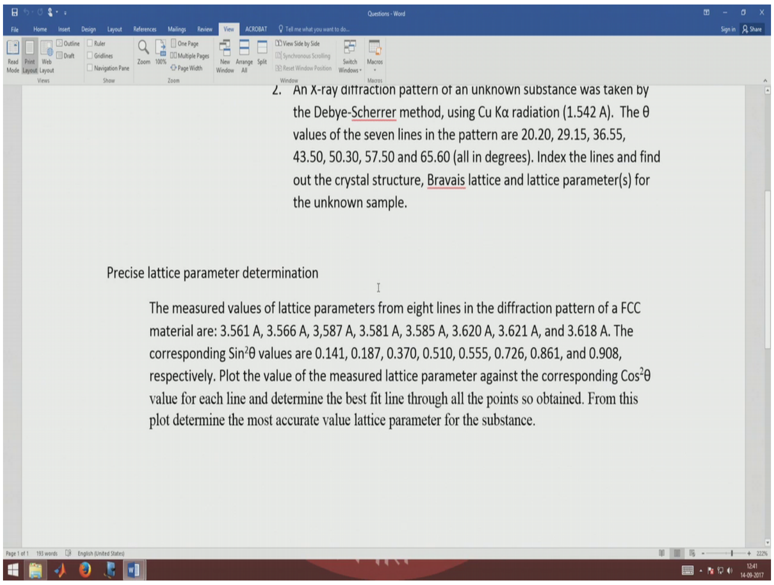

So, the similar exercise, and I will just show you how we are doing it in under another way; the other problem which I am going to show it precise lattice parameter determination.

The problem is the measured values of lattice parameter from the 8 lines in the diffraction pattern of FCC material are 3.56 and refined 566 etcetera, etcetera. And the corresponding sin square theta values are given for all 8 lines plot the value of the measured lattice parameter against the corresponding cos square theta value for each line and determine the best fit line through all the points. So, obtained from this plot determine the most accurate value lattice parameter for the substance.

So, typically this 2 problems, the procedure has been elaborately discussed in the literature, it is the same procedure if you follow on this problem, it will be of some good exercise.

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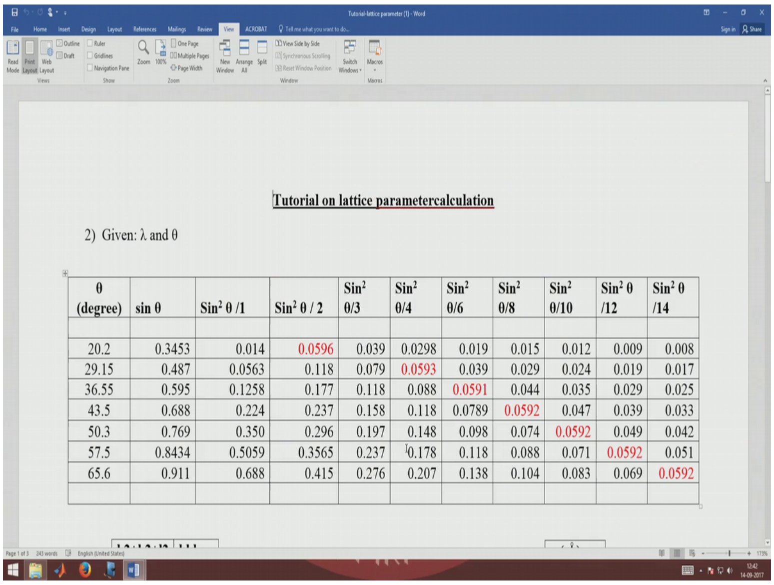

Tutorial on lattice parametercalculation

2) Given: λ and θ

θ (degree)	sin θ	$Sin^2\ \theta$ /1	$Sin^2\ \theta$ / 2	$Sin^2\ \theta$/3	$Sin^2\ \theta$/4	$Sin^2\ \theta$/6	$Sin^2\ \theta$/8	$Sin^2\ \theta$/10	$Sin^2\ \theta$ /12	$Sin^2\ \theta$ /14
20.2	0.3453	0.014	0.0596	0.039	0.0298	0.019	0.015	0.012	0.009	0.008
29.15	0.487	0.0563	0.118	0.079	0.0593	0.039	0.029	0.024	0.019	0.017
36.55	0.595	0.1258	0.177	0.118	0.088	0.0591	0.044	0.035	0.029	0.025
43.5	0.688	0.224	0.237	0.158	0.118	0.0789	0.0592	0.047	0.039	0.033
50.3	0.769	0.350	0.296	0.197	0.148	0.098	0.074	0.0592	0.049	0.042
57.5	0.8434	0.5059	0.3565	0.237	0.178	0.118	0.088	0.071	0.0592	0.051
65.6	0.911	0.688	0.415	0.276	0.207	0.138	0.104	0.083	0.069	0.0592

So, what I have just done is, I have just solved it on the excel sheet. So, in since it is lot of numbers on the table. So, in order to avoid lot of writing on the board, I we have taken in the excel sheet. So, all the theta values are taken, and then you see that sin theta values are shown here, and like what we have discussed in the lecture this is the another way of generating the sin square theta table. For example, if you look at this sin square theta divided by this h k l, you know indices 1 2 3 4 6 8 and so on and if you generate the data like this on each column.

As we have seen in the lecture notes.

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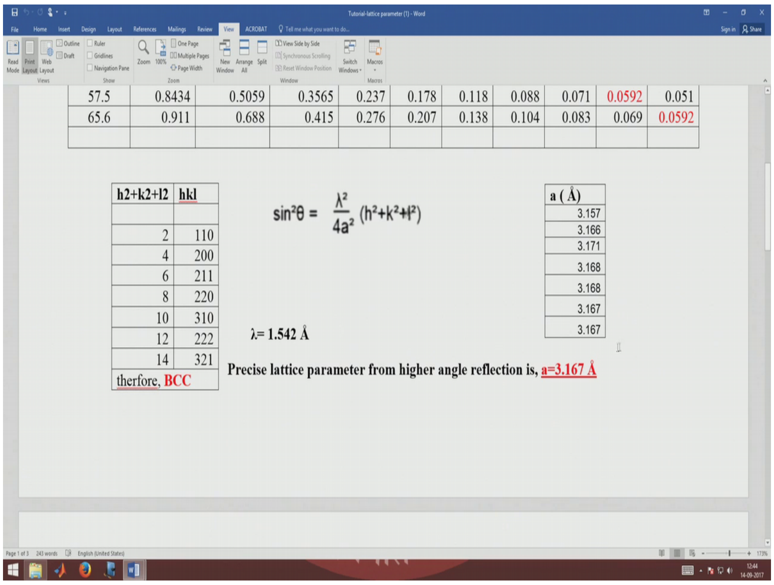

So, the same relation holds here and you see the sin square theta by 2, where you see the 0.0596 value, you are obtaining the similar value, in the sin square theta by 4 in the second number. And similarly you have sin square theta by 6, you see that it is obtained here, and sin square theta by 8 you get the same value. Sin square theta by 10 again you are getting same value. So, if you put all this into a table like h square k square l square, where you see 2 4 6 8 10 12 14 etcetera, etcetera.

If you see that 2 4 6 then, the corresponding the combination of miller indices for 2 is 1 1 0 for 4 is 2 0 0 and so on; so if you can generate this and you will be able to generate this lattice parameter for all the given values using this relation. So, out of this So many lattice parameters the lattice parameter which correspond to higher angle are suppose to be much more accurate, as we have seen in the lecture notes also. This point has been emphasized. So, if you look at this table of lattice constant calculated.

You see that 3.167 is considered the precise lattice parameter from the higher angle of reflection.

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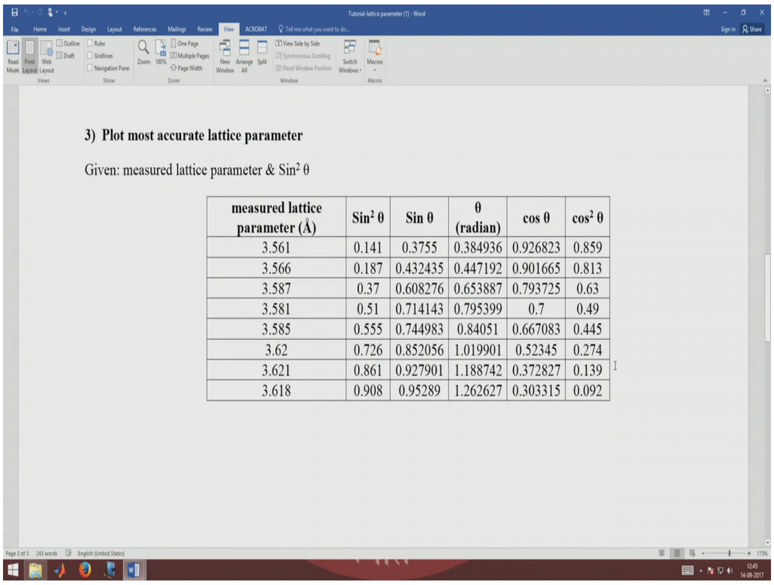
3) Plot most accurate lattice parameter

Given: measured lattice parameter & $Sin^2\,\theta$

measured lattice parameter (Å)	$Sin^2\,\theta$	Sin θ	θ (radian)	cos θ	$cos^2\,\theta$
3.561	0.141	0.3755	0.384936	0.926823	0.859
3.566	0.187	0.432435	0.447192	0.901665	0.813
3.587	0.37	0.608276	0.653887	0.793725	0.63
3.581	0.51	0.714143	0.795399	0.7	0.49
3.585	0.555	0.744983	0.84051	0.667083	0.445
3.62	0.726	0.852056	1.019901	0.52345	0.274
3.621	0.861	0.927901	1.188742	0.372827	0.139
3.618	0.908	0.95289	1.262627	0.303315	0.092

So, that is solves the problem; and if you look at the most accurate lattice parameter calculation. So, we have the measured lattice parameter. And then we have a sin square theta values. And if you from the sin square theta you are calculating sin theta from sin theta to theta, and then you take again a cos theta value and then cos square theta.

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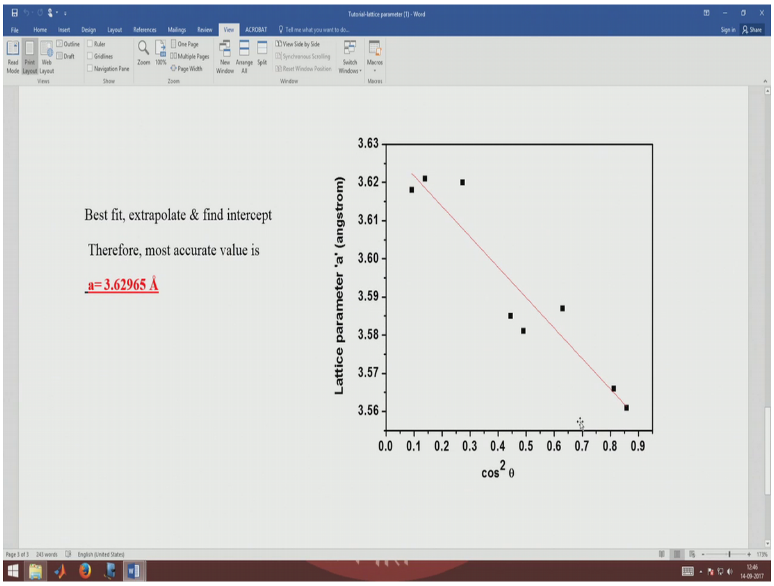

So, the procedure is given in the lecture notes. So, I am not getting into the details again So the same thing. So, what we have to do is we have to just make a plot of lattice parameter versus cos square theta, like this. And then make a best fit like this So, this is the best fit for this data. And extrapolate and find the intercept. So, you have to extrapolate this line and which goes and intercept at the value of 3.629 something close to that. So, you see that the precise lattice parameter is found out from this intercept.

So, that is the exact way of doing this. So, you can also practice similar problems from the various text books, how to find out the precise lattice parameter from the given X-ray data. And also for the determination of crystal structures we have clearly demonstrated in 2 3 problems how to solve it.

I hope you will find this useful in solving this any problem in the future.

Thank you.