INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
NPTEL
NPTEL ONLINE CERTIFICATION COURSE
Structural Analysis of Nanomaterials
Lecture – 13
Determination of Crystal Structures
By XRD Patterns

With

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Hello, our next lecture is on determination of crystal structures by XRD patterns. So before going to start let us know that how it has come so in since 1913,

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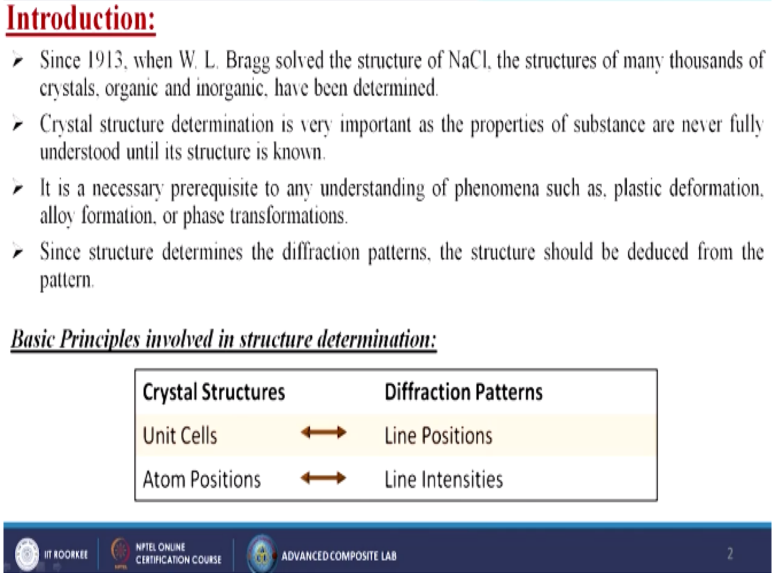

Introduction:

- Since 1913, when W. L. Bragg solved the structure of NaCl, the structures of many thousands of crystals, organic and inorganic, have been determined.
- Crystal structure determination is very important as the properties of substance are never fully understood until its structure is known.
- It is a necessary prerequisite to any understanding of phenomena such as, plastic deformation, alloy formation, or phase transformations.
- Since structure determines the diffraction patterns, the structure should be deduced from the pattern.

Basic Principles involved in structure determination:

Crystal Structures		Diffraction Patterns
Unit Cells	⟷	Line Positions
Atom Positions	⟷	Line Intensities

When W.L. Bragg solved the structure of sodium chloride, the structures of many thousands of crystals organic and inorganic have been determined. Crystal structure determination is very important because as the properties of substance are never fully understood until its structure is known. It is necessary prerequisite to any understanding of phenomena such as the plastic deformation, alloy formations, or phase transformations.

So actually if I want to know that physical property or the chemical properties any kind of materials, so we have to know that crystal structure of that particular materials. Since structure determines the diffraction patterns, the structure should be deduced from the pattern itself. So what are the basic principles involved in structure determinations? So if I talked about the unit cell crystal structure, it is called the line positions, and if we are talking about the atom positions then it is called the line intensities. So first we have to know,

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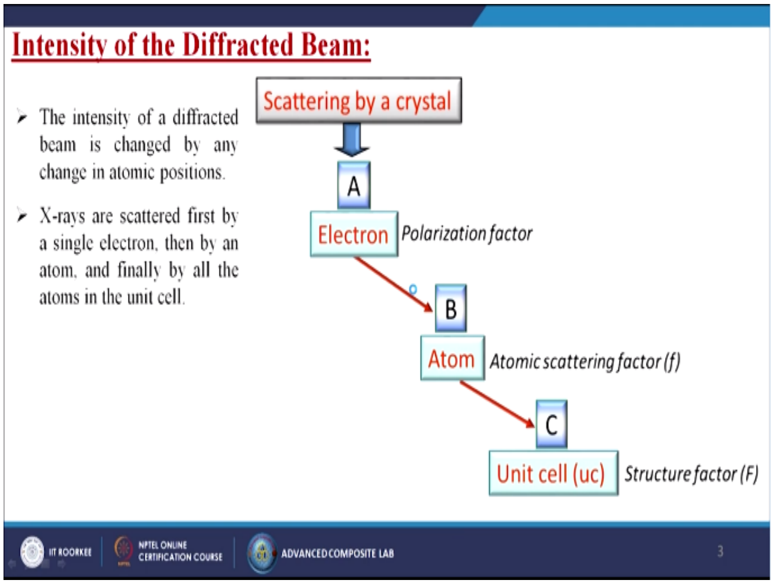

Intensity of the Diffracted Beam:

- The intensity of a diffracted beam is changed by any change in atomic positions.
- X-rays are scattered first by a single electron, then by an atom, and finally by all the atoms in the unit cell.

Scattering by a crystal

A Electron *Polarization factor*

B Atom *Atomic scattering factor (f)*

C Unit cell (uc) *Structure factor (F)*

What is the intensity of the diffracted beam, so generally the intensity of the diffracted beam is changed by any change in the in atomic positions? X-rays which are scattered first by the single electron, then by an atom, and finally by all the atoms in the unit cell, so from here you can see why we are talking about the scattering by a crystals so first electron is coming from that electron we can get the polarization factor.

Then we will talk about the, or maybe we will get the information about atom. So from atom we will get the atomic scattering factor, or maybe in small it is known as the f, and then after that we will get the information about the unit cell or maybe the structure factor.

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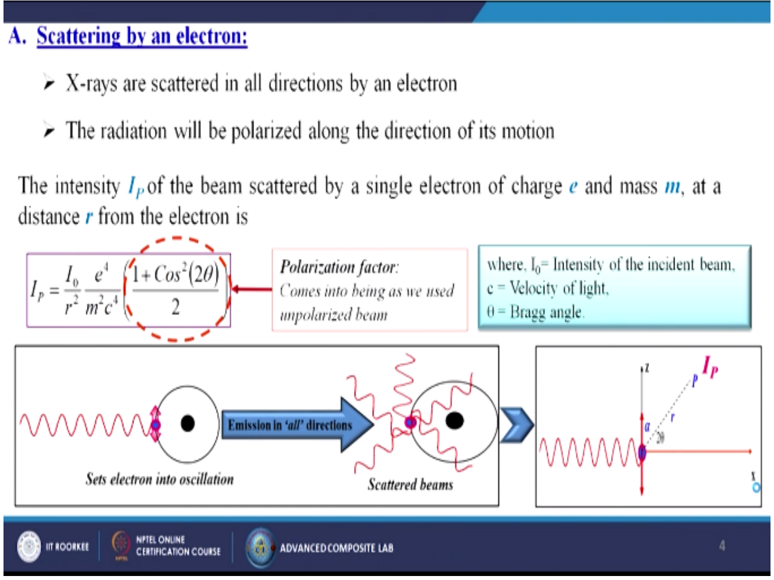

A. Scattering by an electron:

- X-rays are scattered in all directions by an electron
- The radiation will be polarized along the direction of its motion

The intensity I_p of the beam scattered by a single electron of charge e and mass m, at a distance r from the electron is

$$I_P = \frac{I_0}{r^2}\frac{e^4}{m^2c^4}\left(\frac{1+\cos^2(2\theta)}{2}\right)$$

Polarization factor: Comes into being as we used unpolarized beam

where, I_0 = Intensity of the incident beam,
c = Velocity of light,
θ = Bragg angle.

So fist we will discuss about the first sub thing that is the scattering by an electron. So generally the x-ray are scattered in all directions by an electron, the radiations will be polarized along the directions of its motion. So the intensity IP or the beams can scattered by a single electron or charge e, and the mass m at the distance r from the electrons are from the electron is generally IP is equal to I_0 by the r^2 e to the power four by m^2 c to the power four, whole multiplied by 1 plus

Cos square two θ by 2. So in this particular case you can see that one by cos square 2, θ by 2, which is nothing but know as a polarization factor, which comes in to being as we use the UN polarized beam. Where i0 is the intensity of the incident beam, c is the velocity of the light and θ is the Bragg angle.

So from these particular image you can see that electrons is there when the incident is coming to an fall up in the electrons, the electrons starts vibrating then after that the diffraction pattern is going into different directions and from these we are assuming that the diffraction pattern is following the x path and following the z path and we are taking the resultant of that deflected beam.

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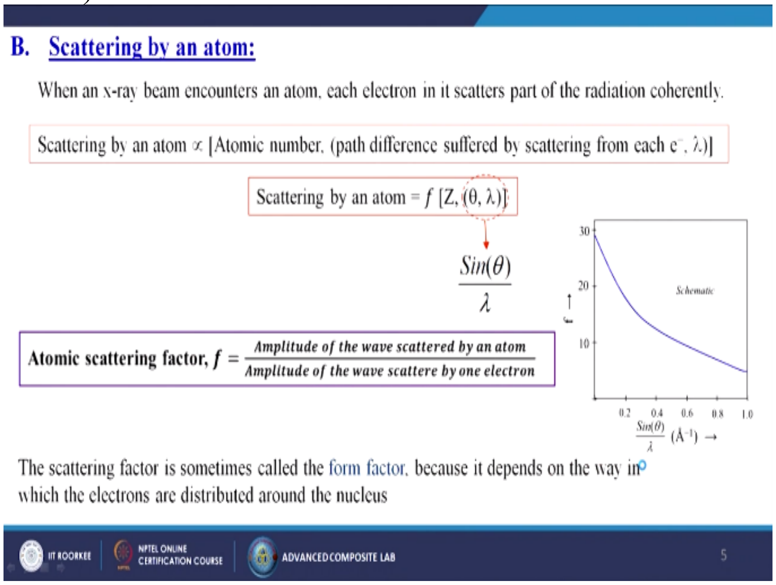

B. Scattering by an atom:

When an x-ray beam encounters an atom, each electron in it scatters part of the radiation coherently.

Scattering by an atom ∝ [Atomic number, (path difference suffered by scattering from each e^-, λ)]

Scattering by an atom = f [Z, (θ, λ)]

$$\frac{Sin(\theta)}{\lambda}$$

Atomic scattering factor, $f = \dfrac{\textit{Amplitude of the wave scattered by an atom}}{\textit{Amplitude of the wave scattere by one electron}}$

The scattering factor is sometimes called the form factor, because it depends on the way in which the electrons are distributed around the nucleus

Now we are going to discuss about the scattering by an atom. So when an x-ray beam encounters an atom, each electron in it scatters part of the radiation coherently. So scattering by an atom which is directly proportional to the atomic number, which is nothing but the path difference suffered by the scattering from the each an electron and the λ which is nothing but the wave length.

So scattering by an atom is equal to f into z θ and λ. So here θ λ is nothing but the relation in between the θ λ is the sign θ by λ. So from the atomics scattering factor if is known as amplitude of the wave scattered by a atom, divided by amplitude of the wave scattered by one electron which we can easily see through by these graph itself, so here in this case the f is increasing and this case sin θ λ per angstrom it is increasing into the x directions.

And from here you can see that the f if it is higher and then if it is going down so automatically the sin θ λ per angstrom is also coming down. So the scattering factor is sometimes called the form factor also, because it depends on the way in which the electrons are distributed around the nucleus.

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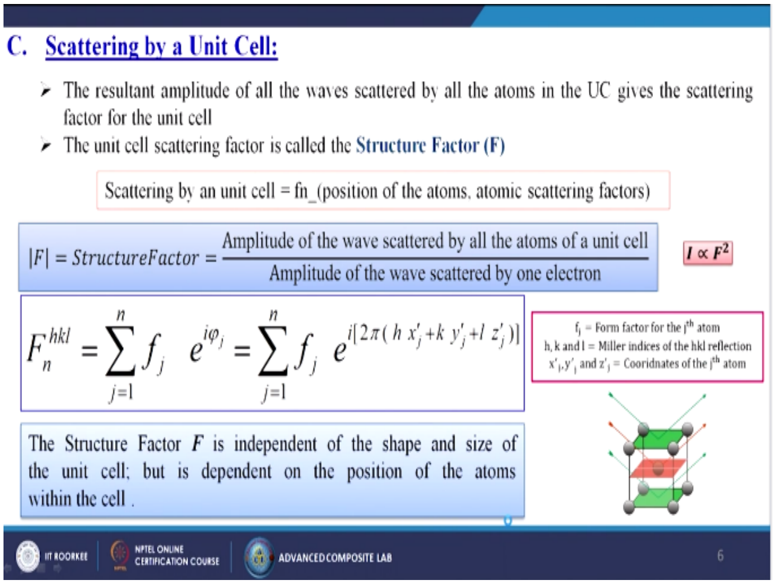

C. Scattering by a Unit Cell:

- The resultant amplitude of all the waves scattered by all the atoms in the UC gives the scattering factor for the unit cell
- The unit cell scattering factor is called the **Structure Factor (F)**

Scattering by an unit cell = fn_(position of the atoms, atomic scattering factors)

$$|F| = StructureFactor = \frac{\text{Amplitude of the wave scattered by all the atoms of a unit cell}}{\text{Amplitude of the wave scattered by one electron}}$$

$I \propto F^2$

$$F_n^{hkl} = \sum_{j=1}^{n} f_j \; e^{i\varphi_j} = \sum_{j=1}^{n} f_j \; e^{i[2\pi(h\,x'_j + k\,y'_j + l\,z'_j)]}$$

f_j = Form factor for the j^{th} atom
h, k and l = Miller indices of the hkl reflection
x'_j, y'_j and z'_j = Cooridnates of the j^{th} atom

The Structure Factor ***F*** is independent of the shape and size of the unit cell; but is dependent on the position of the atoms within the cell .

Next we are going to discuss about the scattering by a unit cell. So the resultant amplitude of all the ways scattered by all the atoms in the unit cell gives the scattering factor for the unit cell. The unit cells scattering factor is also called the structure factor which is nothing but known as capital F, so scattering by a unit cell is equal to the function or positions of the atoms and atomic scattering factors.

So here f magnitude which is nothing but known as structure factor is equal to amplitude of the waves scattered by all the atoms of the unit cell by amplitude of the waves scattered by one electron. So here I, directly proportional to f square, so now we are going to discuss about the F $_n$ ^{hkl} is equal to summation over j is equal to 1 to n, f z which is nothing but the form vector or maybe form factor and then exponential to the i5z is equal to summation over z is equal to 1 to n f z e to the power I in to the 2 pie h x z prime plus k y z prime plus l z j prime.

So in this particular case f j is the form factor for the jth atom, h k and l are the miller indices of the h k l reflections, x j prime y j prime and z j prime is the coordinates of the jth atom. So the structure factor f is independent of the shape and size of the unit cell, but is dependent on the position of the atoms within the cell itself, so what are the methods to determine of an unknown structure processed in three major steps generally. So first the shape and size,

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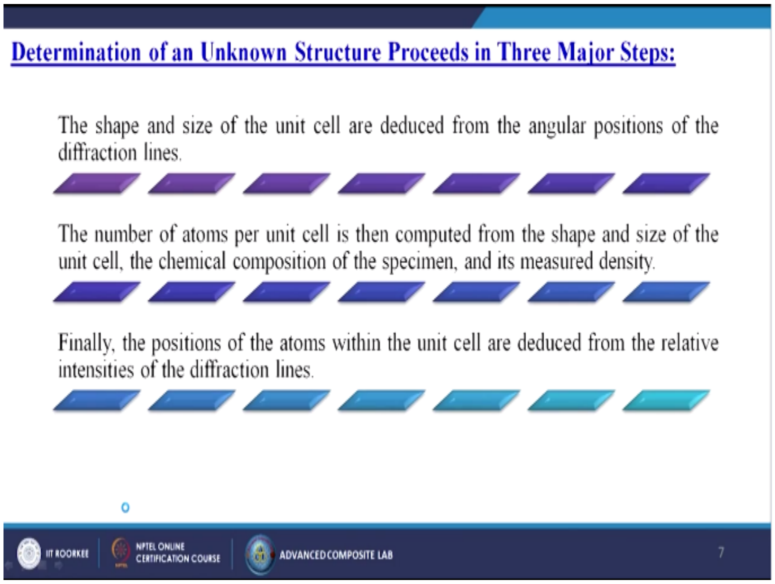

Determination of an Unknown Structure Proceeds in Three Major Steps:

The shape and size of the unit cell are deduced from the angular positions of the diffraction lines.

The number of atoms per unit cell is then computed from the shape and size of the unit cell, the chemical composition of the specimen, and its measured density.

Finally, the positions of the atoms within the unit cell are deduced from the relative intensities of the diffraction lines.

Of the unit cells are deduced from the angular positions of the diffraction lines. Second the number of atoms per unit cell is then computed from the shape and size of the unit cell, the chemical composition of the specimen, and its measured density, and the third is finally the position of the atoms within the unit cell are deduced from the relative intensities of the diffraction lines.

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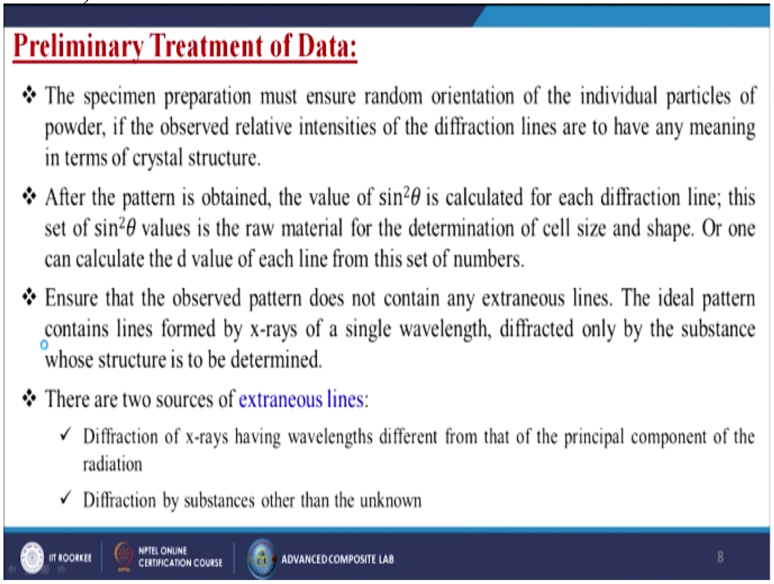

Preliminary Treatment of Data:

- The specimen preparation must ensure random orientation of the individual particles of powder, if the observed relative intensities of the diffraction lines are to have any meaning in terms of crystal structure.
- After the pattern is obtained, the value of $\sin^2\theta$ is calculated for each diffraction line; this set of $\sin^2\theta$ values is the raw material for the determination of cell size and shape. Or one can calculate the d value of each line from this set of numbers.
- Ensure that the observed pattern does not contain any extraneous lines. The ideal pattern contains lines formed by x-rays of a single wavelength, diffracted only by the substance whose structure is to be determined.
- There are two sources of extraneous lines:
  - ✓ Diffraction of x-rays having wavelengths different from that of the principal component of the radiation
  - ✓ Diffraction by substances other than the unknown

So first what we are doing about the preliminary treatment of data. So the specimen preparation must ensure the random orientation of the individual particles of powder, if the observed relative intensities of the diffraction lines are to have any meaning in terms of crystal structure. After the pattern is obtained, the value of sin square θ is calculated for each diffraction line, this set of sin square θ value is the raw material for the determination of the cell size and shape.

Or one can calculate the d value which is interlayer distance of each line from this set of numbers. Ensure that the observed pattern does not contain any extraneous lines. The ideal pattern contains lines formed by x-ray of the single wavelength, diffracted only by the substance whose structure is to be determined because whatever the peeks actually we are getting now we are going to determine or maybe we are going to do the treatment only for those peeks. If there is some extra peeks comes, so that can be possible may be by the two sources, so the first one is known as the diffraction of x- rays having wavelength different from that of the principal component of the radiations and diffraction by substances other than the unknown.

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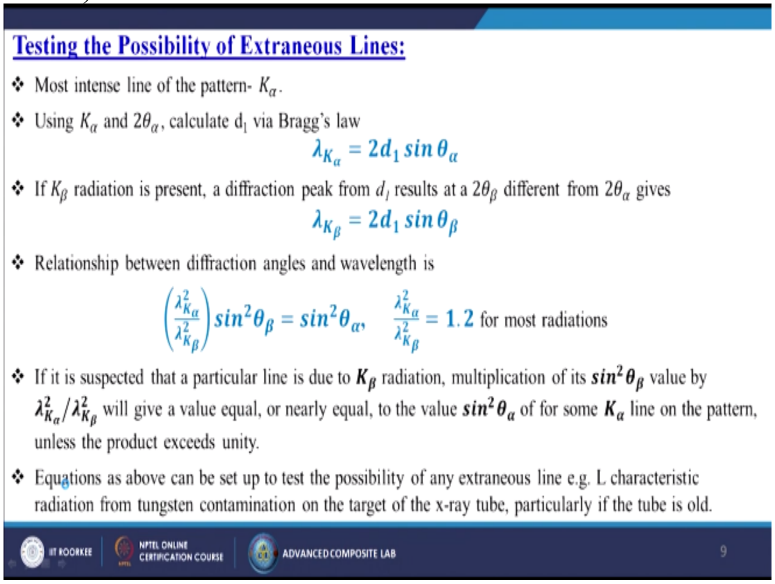

Testing the Possibility of Extraneous Lines:

- Most intense line of the pattern- K_α.
- Using K_α and $2\theta_\alpha$, calculate d_1 via Bragg's law

$$\lambda_{K_\alpha} = 2d_1 \sin\theta_\alpha$$

- If K_β radiation is present, a diffraction peak from d_l results at a $2\theta_\beta$ different from $2\theta_\alpha$ gives

$$\lambda_{K_\beta} = 2d_1 \sin\theta_\beta$$

- Relationship between diffraction angles and wavelength is

$$\left(\frac{\lambda^2_{K_\alpha}}{\lambda^2_{K_\beta}}\right)\sin^2\theta_\beta = \sin^2\theta_\alpha, \quad \frac{\lambda^2_{K_\alpha}}{\lambda^2_{K_\beta}} = 1.2 \text{ for most radiations}$$

- If it is suspected that a particular line is due to K_β radiation, multiplication of its $\sin^2\theta_\beta$ value by $\lambda^2_{K_\alpha}/\lambda^2_{K_\beta}$ will give a value equal, or nearly equal, to the value $\sin^2\theta_\alpha$ of for some K_α line on the pattern, unless the product exceeds unity.
- Equations as above can be set up to test the possibility of any extraneous line e.g. L characteristic radiation from tungsten contamination on the target of the x-ray tube, particularly if the tube is old.

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So now we are going to discuss about that testing the possibility of the extraneous lines, why it may occur? So most intense line of the pattern is the k α using k α and 2 θ αs calculate the d1 by the Braggs law which is nothing but the λ k α is equal to 2 d1 sin θ α. If k beta radiation is present, that's why in our previous lectures we have already been discussed that we are going to use some kind of filters to restrict the other kind of radiations over there.

So if k beta radiation is present the diffraction peek from d1 result at it 2 θ beta different from 2 θ α gives like λ k beta is equal to 2 d1 sin θ b. relationship between the diffraction angles and wavelength is λ square k α by λ square k beta in to sin square θ beta is equal to sin square θ α. So generally λ square k α by λ square k beta is around 1.2 for most of the radiations.

If it is suspected that a particular line is due to k beta radiations multiplication of its sin square θ beta value by λ square k α by λ square k beta will give you a value equal or maybe the near equal or to the value of sin square θ α for some k α line on the pattern unless the product exceeds the unity.

Equation as above can be set up to test the possibility of any extraneous lines like L characteristic radiation from tungsten contamination on the target of the x-ray tube, particularly if the tube is old. So that time maybe some kind of extraneous lines can be generated due to that the own out tube of the tungsten. So now we are going to discuss about the relations between,

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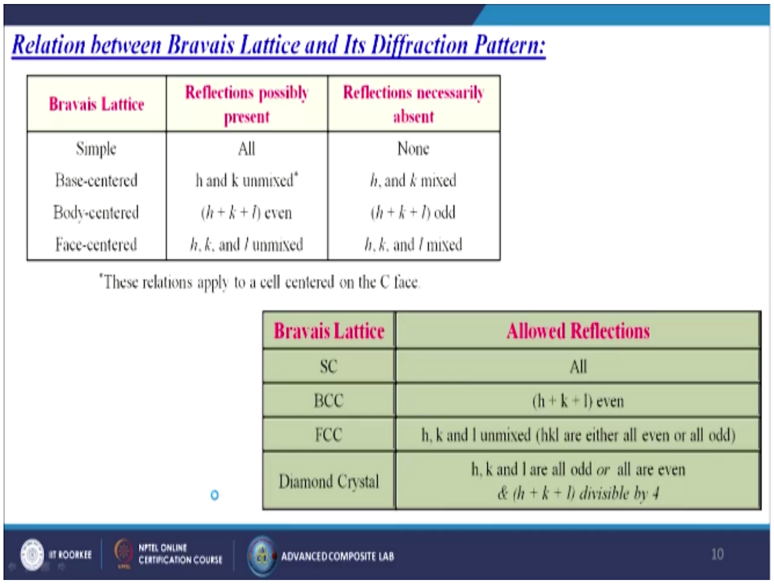

Relation between Bravais Lattice and Its Diffraction Pattern:

Bravais Lattice	Reflections possibly present	Reflections necessarily absent
Simple	All	None
Base-centered	h and k unmixed*	*h*, and *k* mixed
Body-centered	$(h + k + l)$ even	$(h + k + l)$ odd
Face-centered	*h*, *k*, and *l* unmixed	*h*, *k*, and *l* mixed

*These relations apply to a cell centered on the C face.

Bravais Lattice	Allowed Reflections
SC	All
BCC	(h + k + l) even
FCC	h, k and l unmixed (hkl are either all even or all odd)
Diamond Crystal	h, k and l are all odd *or* all are even *& $(h + k + l)$ divisible by 4*

Bravais lattice and its diffraction pattern, so generally if the bravais lattice is simple then reflection possibly present in all, reflections necessarily absent is almost its vice versa that means none for base centered generally h and k will be the un mixed one but this relations applied to the cells centered on a c face and for the absent here h and k will be the mixed one. For the body centered each k and l the summation of h k and l will be the even one, and for the absents here h plus k plus l will be the odd one, for the face centered h k and l will be unmixed but for the absent here will get the h k and l all are in mixed conditions.

So if we see that actually what will is the allowable reflections for any crystal, so generally for the single crystals it is all for BCC the summations of h plus k plus l is even, for FCC h k and l is unmixed that means h k l all maybe either even or maybe all are odd. And for the diamond crystals h, k and l are all odd or maybe all are even or maybe h plus k plus l which is the summations of h plus k plus l will be divisible by the 4.

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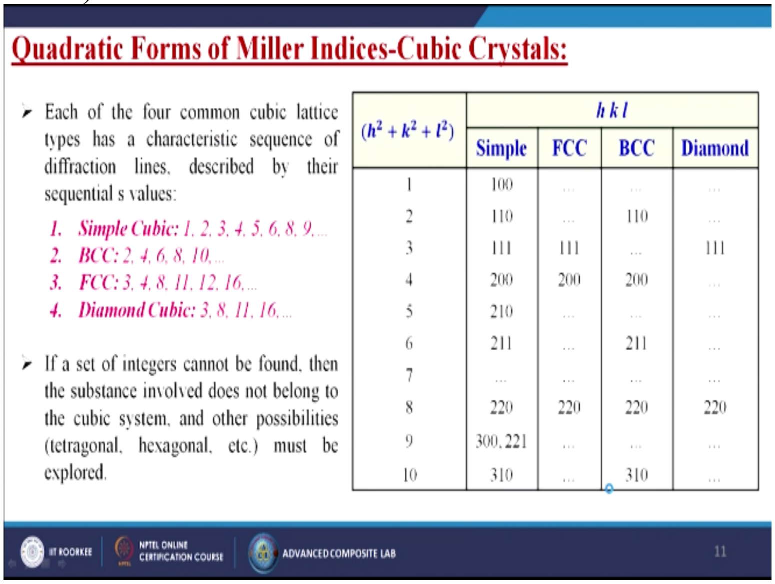

Quadratic Forms of Miller Indices-Cubic Crystals:

- Each of the four common cubic lattice types has a characteristic sequence of diffraction lines, described by their sequential s values:
  1. *Simple Cubic: 1, 2, 3, 4, 5, 6, 8, 9,…*
  2. *BCC: 2, 4, 6, 8, 10,…*
  3. *FCC: 3, 4, 8, 11, 12, 16,…*
  4. *Diamond Cubic: 3, 8, 11, 16,…*
- If a set of integers cannot be found, then the substance involved does not belong to the cubic system, and other possibilities (tetragonal, hexagonal, etc.) must be explored.

$(h^2 + k^2 + l^2)$	*h k l*			
	Simple	FCC	BCC	Diamond
1	100	…	…	…
2	110	…	110	…
3	111	111	…	111
4	200	200	200	…
5	210	…	…	…
6	211	…	211	…
7	…	…	…	…
8	220	220	220	220
9	300, 221	…	…	…
10	310	…	310	…

Now we are going to discuss about the quadratic forms of miller indices for the cubic crystals. So each of the four common cubic lattice types has a characteristic sequence of diffraction lines, described by their sequential s values, like for the single cubic it is 1 2 3 4 5 6 8 9 and so on. For the BCC it should be 2 4 6 8 10. For FCC generally it is 3 4 8 11 12 and 16. And for the diamond cubic it should be 3 8 11 16.

So in this particular case what we are going to do, if a set of integers cannot be found, then the substances involved does not belong to the cubic system, and the other possibilities maybe some other formation like tetragonal and hexagonal can be obtained or maybe must be explored. So here right hand side you can see the h square plus k square plus l square is like 1 2 3 4 5 6 7 8 9 10, so for simple it should be 100, there it should not be any FCC BCC or may be dimension for 2 it is 110 or maybe BCC also it may be present like 110.

Say suppose when we are talking about the seven because 7 is not present because any how the A square k square plus l square value is the summation h square plus k square plus l square is not equal to seven. So that is why for seven it is totally silent and if it is 9 it maybe 300 or maybe 211, or maybe 221.

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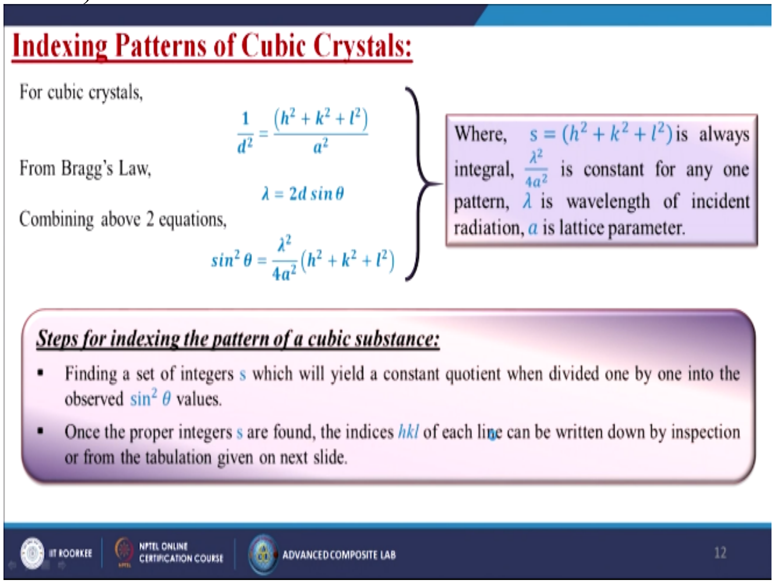

Indexing Patterns of Cubic Crystals:

For cubic crystals,

$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2)}{a^2}$$

From Bragg's Law,

$$\lambda = 2d \sin\theta$$

Combining above 2 equations,

$$\sin^2\theta = \frac{\lambda^2}{4a^2}(h^2 + k^2 + l^2)$$

Where, $s = (h^2 + k^2 + l^2)$ is always integral, $\frac{\lambda^2}{4a^2}$ is constant for any one pattern, λ is wavelength of incident radiation, a is lattice parameter.

Steps for indexing the pattern of a cubic substance:

- Finding a set of integers s which will yield a constant quotient when divided one by one into the observed $\sin^2\theta$ values.
- Once the proper integers s are found, the indices *hkl* of each line can be written down by inspection or from the tabulation given on next slide.

Indexing patterns of the cubic crystals: so for the cubic crystals, generally indexing patterns is like this 1 by D Square is equal to H Square plus k square plus l square by a^2 from Braggs law, we know that λ is equal to 2b sin θ. So combining these one and these s4econd equations, we can get sin square θ is equal to λ square by 4 A square plus h square plus k square plus l square.

So were s generally we are denoting A square plus k square plus l square as a smallest is always it is an integral and then λ square by 4a square is constant for any one pattern, λ is wavelength of incident radiations and A is the lattice parameter. So now we are going to discuss that how we are going to calculate all this things. So steps for indexing the pattern of cubic substance, finding a set of integers which will yield a constant quotient when divided one by one into the observed sin square θ values. Once the proper integer5s s are found, the indices h k l, of each line can be written down by inspection or from the tabulation given in the next slide.

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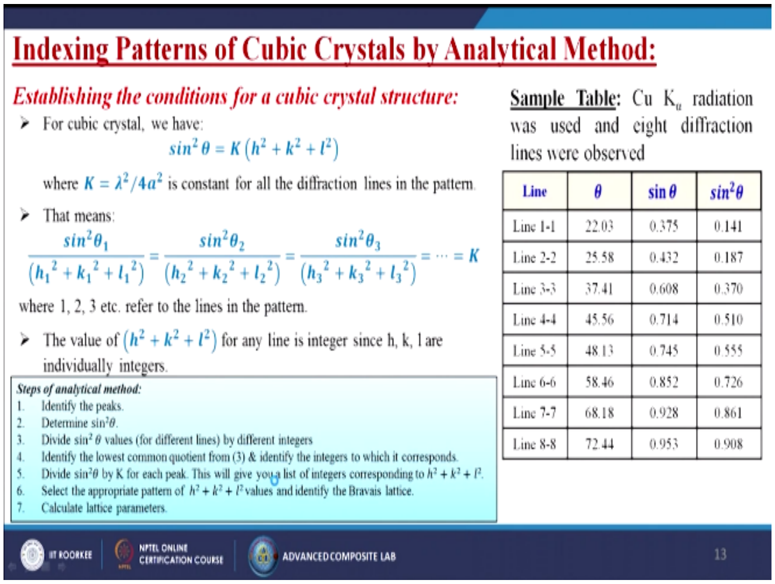

Indexing Patterns of Cubic Crystals by Analytical Method:

Establishing the conditions for a cubic crystal structure:

- For cubic crystal, we have:

$$\sin^2\theta = K\left(h^2 + k^2 + l^2\right)$$

where $K = \lambda^2/4a^2$ is constant for all the diffraction lines in the pattern.

- That means:

$$\frac{\sin^2\theta_1}{\left(h_1{}^2 + k_1{}^2 + l_1{}^2\right)} = \frac{\sin^2\theta_2}{\left(h_2{}^2 + k_2{}^2 + l_2{}^2\right)} = \frac{\sin^2\theta_3}{\left(h_3{}^2 + k_3{}^2 + l_3{}^2\right)} = \cdots = K$$

where 1, 2, 3 etc. refer to the lines in the pattern.

- The value of $\left(h^2 + k^2 + l^2\right)$ for any line is integer since h, k, l are individually integers.

Steps of analytical method:

1. Identify the peaks.
2. Determine $\sin^2\theta$.
3. Divide $\sin^2\theta$ values (for different lines) by different integers
4. Identify the lowest common quotient from (3) & identify the integers to which it corresponds.
5. Divide $\sin^2\theta$ by K for each peak. This will give you a list of integers corresponding to $h^2 + k^2 + l^2$.
6. Select the appropriate pattern of $h^2 + k^2 + l^2$ values and identify the Bravais lattice.
7. Calculate lattice parameters.

Sample Table: Cu K_α radiation was used and eight diffraction lines were observed

Line	θ	$\sin\theta$	$\sin^2\theta$
Line 1-1	22.03	0.375	0.141
Line 2-2	25.58	0.432	0.187
Line 3-3	37.41	0.608	0.370
Line 4-4	45.56	0.714	0.510
Line 5-5	48.13	0.745	0.555
Line 6-6	58.46	0.852	0.726
Line 7-7	68.18	0.928	0.861
Line 8-8	72.44	0.953	0.908

So now we are going to discuss about the indexing patterns of cubic crystals by analytical methods: so before going to start, first we have to establishing the condition for a cubic crystal structure, so for cubic crystals generally we are having sin square θ is equal to capital K into A square plus k square plus l square, where the k is the constant that means its equal to λ square by 4a square.

So now that means, the sin square θ one by h1 square plus k1 square plus l1 square is equal to the θ two for each 2 k, 2l2 and so on, because which all are the constant value. So weir 1 2 3 etc, referred to the lines of the pattern. So the value of h square plus k square plus l square for any line is integer since h k l are individually integers. So in this case we have A actually mentioned all the steps for these analytical methods.

Which I am going to discuss by slide by slide, so in this case simple we have taken upper k α radiations value and from that jus we are going to give an example, So here in this particular case we are having line 11 we are having some θ value. So we are having θ value means, these all are the obtained peeks from the x or d θ.

So from that particular peeks we are getting the θ value then we are making it a sin θ and the sin square θ value. Then after that what we are doing? We are doing these sin square θ by the integers like divided by integers 1,2,34,5,6,810,9, like that, and then we are trying to get the common value that which is matching with the line 11 or maybe line 22 or maybe line 22 with line 33, so in this particular case you can see that for line 11 the sin square θ divided by three is value is 0.0469.

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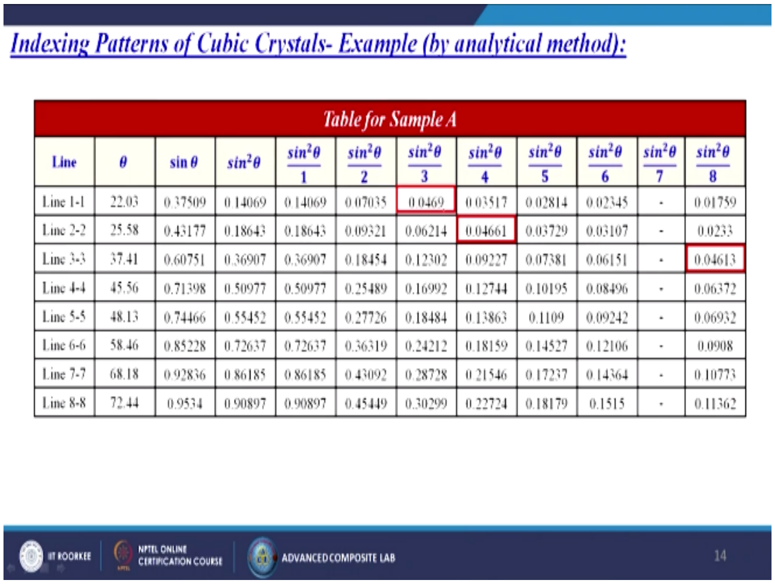

Indexing Patterns of Cubic Crystals- Example (by analytical method):

Table for Sample A

Line	θ	$\sin\theta$	$\sin^2\theta$	$\frac{\sin^2\theta}{1}$	$\frac{\sin^2\theta}{2}$	$\frac{\sin^2\theta}{3}$	$\frac{\sin^2\theta}{4}$	$\frac{\sin^2\theta}{5}$	$\frac{\sin^2\theta}{6}$	$\frac{\sin^2\theta}{7}$	$\frac{\sin^2\theta}{8}$
Line 1-1	22.03	0.37509	0.14069	0.14069	0.07035	0.0469	0.03517	0.02814	0.02345	-	0.01759
Line 2-2	25.58	0.43177	0.18643	0.18643	0.09321	0.06214	0.04661	0.03729	0.03107	-	0.0233
Line 3-3	37.41	0.60751	0.36907	0.36907	0.18454	0.12302	0.09227	0.07381	0.06151	-	0.04613
Line 4-4	45.56	0.71398	0.50977	0.50977	0.25489	0.16992	0.12744	0.10195	0.08496	-	0.06372
Line 5-5	48.13	0.74466	0.55452	0.55452	0.27726	0.18484	0.13863	0.1109	0.09242	-	0.06932
Line 6-6	58.46	0.85228	0.72637	0.72637	0.36319	0.24212	0.18159	0.14527	0.12106	-	0.0908
Line 7-7	68.18	0.92836	0.86185	0.86185	0.43092	0.28728	0.21546	0.17237	0.14364	-	0.10773
Line 8-8	72.44	0.9534	0.90897	0.90897	0.45449	0.30299	0.22724	0.18179	0.1515	-	0.11362

Which is more or less similar to the line 22 why you are dividing the sin square θ value by the 4, and same thing is happening for line 331 while you dividing by the sin square θ by 8. So like these way we are going up to line 88. And then when we are getting line 88 so all the common values say suppose for these examples we are getting the 11, 11 means what? H square plus k square plus l square will be the 11, so that means we are taking it as a 113 because one square plus one square plus three square, the whole summation is 11.

And then the next step also if you see this one for the line 6, we are making it has 400, because it has been divided by the 16. So h square plus k square plus l square is 16, so 4square plus zero square plus zero squares the whole summation is 16. So how now we have to see that the characteristic sequence of the diffraction is matching with which crystal structure. So in this case we are getting 3,4,811,12,16,19,20 that mean it matching with the FCC crystal structure so we can roughly tell that the material is FCC in nature.

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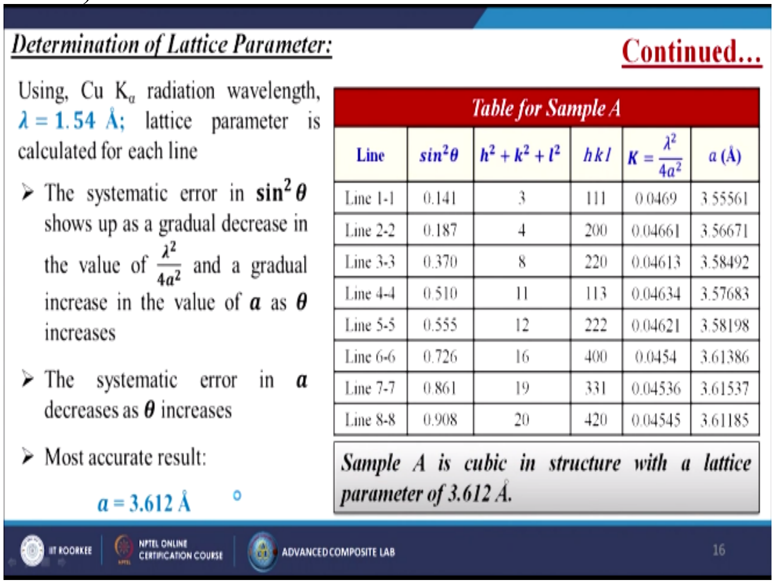


Determination of Lattice Parameter:

Continued...

Using, Cu K_α radiation wavelength, $\lambda = 1.54$ Å; lattice parameter is calculated for each line

- The systematic error in $\sin^2\theta$ shows up as a gradual decrease in the value of $\frac{\lambda^2}{4a^2}$ and a gradual increase in the value of a as θ increases
- The systematic error in a decreases as θ increases
- Most accurate result:

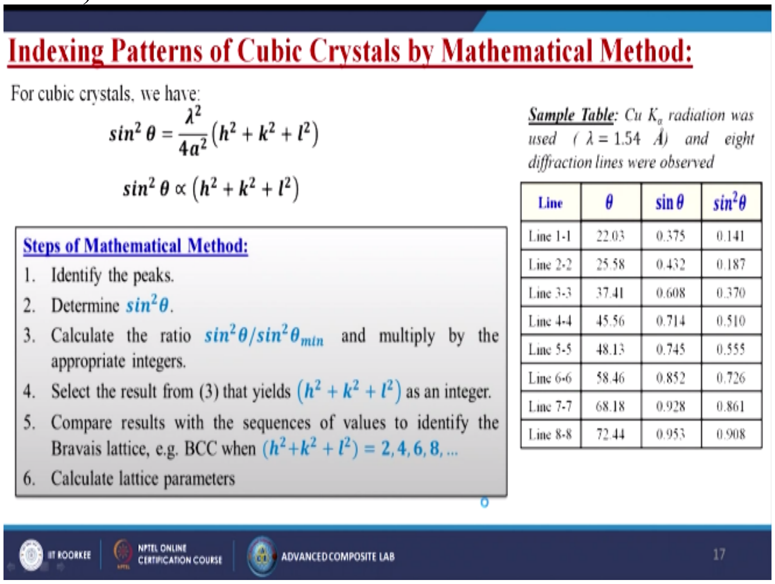
$a = 3.612$ Å

Table for Sample A

Line	$\sin^2\theta$	$h^2+k^2+l^2$	hkl	$K = \frac{\lambda^2}{4a^2}$	a (Å)
Line 1-1	0.141	3	111	0.0469	3.55561
Line 2-2	0.187	4	200	0.04661	3.56671
Line 3-3	0.370	8	220	0.04613	3.58492
Line 4-4	0.510	11	113	0.04634	3.57683
Line 5-5	0.555	12	222	0.04621	3.58198
Line 6-6	0.726	16	400	0.0454	3.61386
Line 7-7	0.861	19	331	0.04536	3.61537
Line 8-8	0.908	20	420	0.04545	3.61185

Sample A is cubic in structure with a lattice parameter of 3.612 Å.

Now in the next slides we are going to discuss about the determinations of the lattice parameters. So in this particular case from the last slide we have already received the value A, square plus KL square plus l square. Now we are already obtained from that value that h k l value of that one, now we are going to get the k value. So the k value means, which is λ square by 4a square, λ value already we know, we know the value of k so we are getting the value of A. So here A is the lattice parameters which we are getting as 3.612 angstrom.
(Refer Slide Time: 20:12)



Indexing Patterns of Cubic Crystals by Mathematical Method:

For cubic crystals, we have:

$$\sin^2\theta = \frac{\lambda^2}{4a^2}\left(h^2+k^2+l^2\right)$$

$$\sin^2\theta \propto \left(h^2+k^2+l^2\right)$$

Steps of Mathematical Method:

1. Identify the peaks.
2. Determine $\sin^2\theta$.
3. Calculate the ratio $\sin^2\theta/\sin^2\theta_{min}$ and multiply by the appropriate integers.
4. Select the result from (3) that yields $\left(h^2+k^2+l^2\right)$ as an integer.
5. Compare results with the sequences of values to identify the Bravais lattice, e.g. BCC when $\left(h^2+k^2+l^2\right) = 2, 4, 6, 8, \ldots$
6. Calculate lattice parameters

Sample Table: *Cu K_α radiation was used ($\lambda = 1.54$ Å) and eight diffraction lines were observed*

Line	θ	$\sin\theta$	$\sin^2\theta$
Line 1-1	22.03	0.375	0.141
Line 2-2	25.58	0.432	0.187
Line 3-3	37.41	0.608	0.370
Line 4-4	45.56	0.714	0.510
Line 5-5	48.13	0.745	0.555
Line 6-6	58.46	0.852	0.726
Line 7-7	68.18	0.928	0.861
Line 8-8	72.44	0.953	0.908

Next we are going to discuss about the indexing patterns of cubic crystals by the mathematical method: till now we are discussing about the analytical methods, now we are going to prove the same thing by the mathematics. So for cubic crystals we are having that equations sin square θ is equal to λ square by 4a square into A, square plus k square plus l square. So if we think it's as a constant means capital k that means sin square θ is directly proportional to the A square plus k square plus l square, so in this particular case what we are doing?

We are following the same thing, we are getting the θ value then we are making it has a sin θ and we are making it as a sin square θ also, so in this particular slide we have reached up to these point. After that what we are going to do? We are going to do the sin square θ value by divided by the sin square θ minimum value and multiply by the appropriate integers like 1,2,3,4 like that. And then select the result that is h square plus k square plus l square which I am going to discuss in to the next slide.

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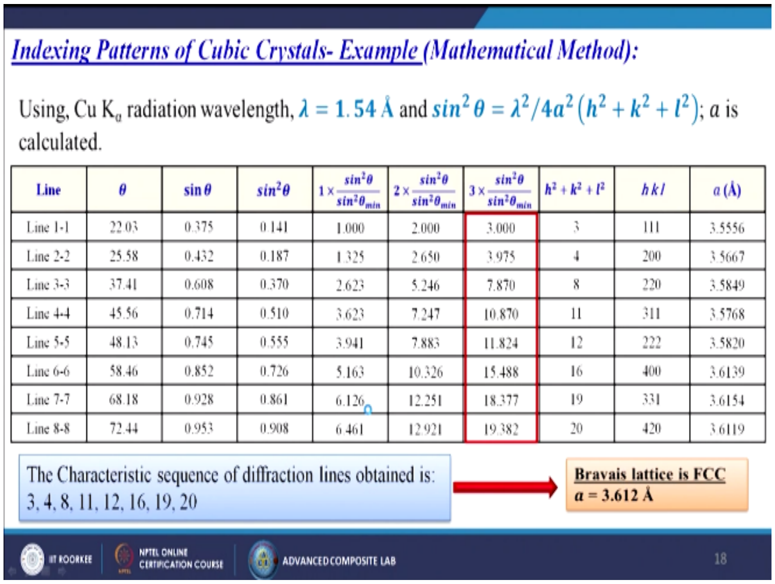

Indexing Patterns of Cubic Crystals- Example (Mathematical Method):

Using, Cu K_α radiation wavelength, $\lambda = 1.54$ Å and $sin^2\theta = \lambda^2/4a^2(h^2+k^2+l^2)$; a is calculated.

Line	θ	$\sin\theta$	$sin^2\theta$	$1\times\frac{sin^2\theta}{sin^2\theta_{min}}$	$2\times\frac{sin^2\theta}{sin^2\theta_{min}}$	$3\times\frac{sin^2\theta}{sin^2\theta_{min}}$	$h^2+k^2+l^2$	hkl	a (Å)
Line 1-1	22.03	0.375	0.141	1.000	2.000	3.000	3	111	3.5556
Line 2-2	25.58	0.432	0.187	1.325	2.650	3.975	4	200	3.5667
Line 3-3	37.41	0.608	0.370	2.623	5.246	7.870	8	220	3.5849
Line 4-4	45.56	0.714	0.510	3.623	7.247	10.870	11	311	3.5768
Line 5-5	48.13	0.745	0.555	3.941	7.883	11.824	12	222	3.5820
Line 6-6	58.46	0.852	0.726	5.163	10.326	15.488	16	400	3.6139
Line 7-7	68.18	0.928	0.861	6.126	12.251	18.377	19	331	3.6154
Line 8-8	72.44	0.953	0.908	6.461	12.921	19.382	20	420	3.6119

The Characteristic sequence of diffraction lines obtained is: 3, 4, 8, 11, 12, 16, 19, 20

Bravais lattice is FCC
$a = 3.612$ Å

So in this particular case what happen? We are getting the sin square θ value then we are dividing these sin square θ value with the minimum sin square θ value. And then we are getting these parameters then that is multiplied in to different integers like 1, 2 and 3, and then from that we are getting the A square plus k square plus h l square value, so from these we are getting the HKL value, and if we get the HKL value, and if we put the HKL value over here.

So from this particular equation we can get the value of A or maybe the lattice parameters. So the characteristics sequence of diffraction lines here also obtain the same thing 3,4,8,11,12,16,19,20 like that and here also the bravais lattice we are founding for these FCC is A is equal to 3.612 angstrom.

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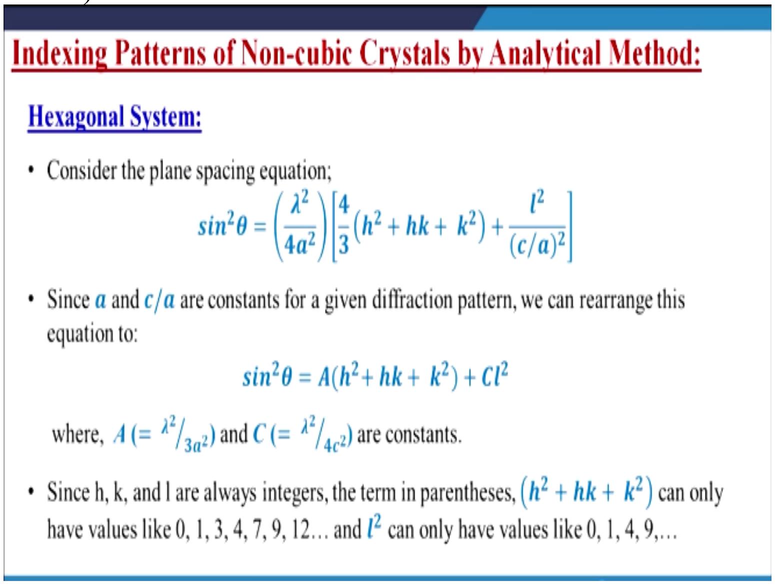

Indexing Patterns of Non-cubic Crystals by Analytical Method:

Hexagonal System:

- Consider the plane spacing equation;

$$sin^2\theta = \left(\frac{\lambda^2}{4a^2}\right)\left[\frac{4}{3}(h^2+hk+k^2)+\frac{l^2}{(c/a)^2}\right]$$

- Since a and c/a are constants for a given diffraction pattern, we can rearrange this equation to:

$$sin^2\theta = A(h^2+hk+k^2)+Cl^2$$

where, $A\,(=\lambda^2/3a^2)$ and $C\,(=\lambda^2/4c^2)$ are constants.

- Since h, k, and l are always integers, the term in parentheses, (h^2+hk+k^2) can only have values like 0, 1, 3, 4, 7, 9, 12… and l^2 can only have values like 0, 1, 4, 9,…

So now we are going to discuss still now discussing about the cubic crystals, now we are going to discuss about the non cubic crystals by this two methods, one is analytical and another one is the mathematical model. So generally for the hexagonal crystals the plane spacing equation is sin square θ is equal to λ square in to 4a square multiplied by 4 by 3, h square plus hk plus k square

plus l square by c by A whole square. So in this case A and c by A or constants for given diffraction patterns we can if we rearrange this equations, we can get sin square θ A, so capital A here is nothing but the λ square by the 3a square and here we are confirming this C which is nothing but the λ square by the 4c square which are the constant.
So since h k and l are always integers that term in parentheses like h square plus h k plus k square can only have value like 0,1,3,4,7,9,12 and l square only have values like 0,1,4,9 etc.
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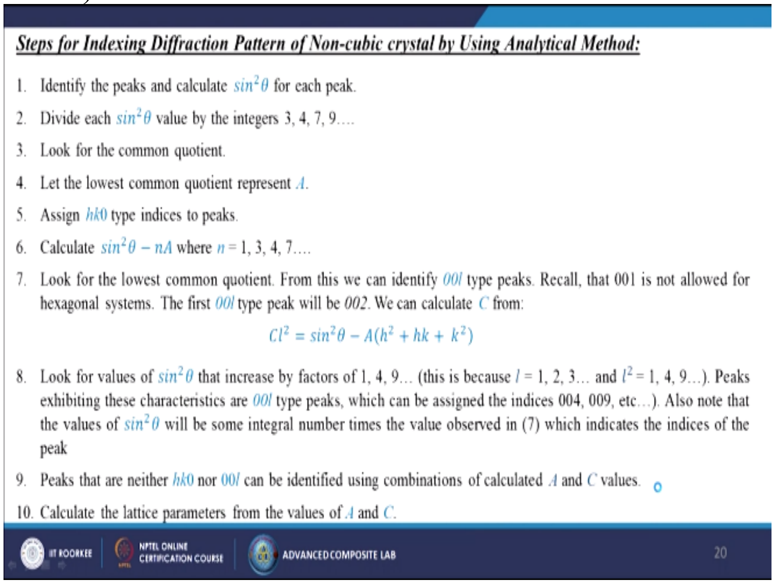

Steps for Indexing Diffraction Pattern of Non-cubic crystal by Using Analytical Method:

1. Identify the peaks and calculate $sin^2\theta$ for each peak.
2. Divide each $sin^2\theta$ value by the integers 3, 4, 7, 9….
3. Look for the common quotient.
4. Let the lowest common quotient represent A.
5. Assign $hk0$ type indices to peaks.
6. Calculate $sin^2\theta - nA$ where $n = 1, 3, 4, 7…$.
7. Look for the lowest common quotient. From this we can identify $00l$ type peaks. Recall, that 001 is not allowed for hexagonal systems. The first $00l$ type peak will be 002. We can calculate C from:

$$Cl^2 = sin^2\theta - A(h^2 + hk + k^2)$$

8. Look for values of $sin^2\theta$ that increase by factors of 1, 4, 9… (this is because $l = 1, 2, 3…$ and $l^2 = 1, 4, 9…$). Peaks exhibiting these characteristics are $00l$ type peaks, which can be assigned the indices 004, 009, etc…). Also note that the values of $sin^2\theta$ will be some integral number times the value observed in (7) which indicates the indices of the peak
9. Peaks that are neither $hk0$ nor $00l$ can be identified using combinations of calculated A and C values.
10. Calculate the lattice parameters from the values of A and C.

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So now here are the steps for the analytical methods. So here also the same thing like the cubic crystals we have written all the steps and we will follow all these steps for next time calculations. So first initially you have to calculate the sin square θ for the each peek so in this case we have,
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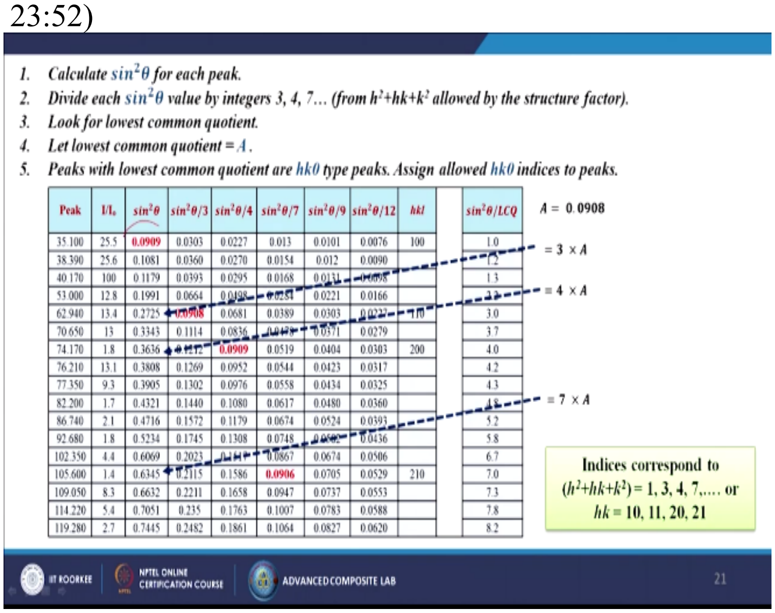

1. *Calculate $sin^2\theta$ for each peak.*
2. *Divide each $sin^2\theta$ value by integers 3, 4, 7… (from h^2+hk+k^2 allowed by the structure factor).*
3. *Look for lowest common quotient.*
4. *Let lowest common quotient = A.*
5. *Peaks with lowest common quotient are $hk0$ type peaks. Assign allowed $hk0$ indices to peaks.*

Peak	I/I₀	$sin^2\theta$	$sin^2\theta/3$	$sin^2\theta/4$	$sin^2\theta/7$	$sin^2\theta/9$	$sin^2\theta/12$	hkl		$sin^2\theta/LCQ$
35.100	25.5	0.0909	0.0303	0.0227	0.013	0.0101	0.0076	100		1.0
38.390	25.6	0.1081	0.0360	0.0270	0.0154	0.012	0.0090			1.2
40.170	100	0.1179	0.0393	0.0295	0.0168	0.0131	0.0098			1.3
53.000	12.8	0.1991	0.0664	0.0498	0.0284	0.0221	0.0166			2.2
62.940	13.4	0.2725	0.0908	0.0681	0.0389	0.0303	0.0227	110		3.0
70.650	13	0.3343	0.1114	0.0836	0.0478	0.0371	0.0279			3.7
74.170	1.8	0.3636	0.1212	0.0909	0.0519	0.0404	0.0303	200		4.0
76.210	13.1	0.3808	0.1269	0.0952	0.0544	0.0423	0.0317			4.2
77.350	9.3	0.3905	0.1302	0.0976	0.0558	0.0434	0.0325			4.3
82.200	1.7	0.4321	0.1440	0.1080	0.0617	0.0480	0.0360			4.8
86.740	2.1	0.4716	0.1572	0.1179	0.0674	0.0524	0.0393			5.2
92.680	1.8	0.5234	0.1745	0.1308	0.0748	0.0582	0.0436			5.8
102.350	4.4	0.6069	0.2023	0.1517	0.0867	0.0674	0.0506			6.7
105.600	1.4	0.6345	0.2115	0.1586	0.0906	0.0705	0.0529	210		7.0
109.050	8.3	0.6632	0.2211	0.1658	0.0947	0.0737	0.0553			7.3
114.220	5.4	0.7051	0.235	0.1763	0.1007	0.0783	0.0588			7.8
119.280	2.7	0.7445	0.2482	0.1861	0.1064	0.0827	0.0620			8.2

$A = 0.0908$

$= 3 \times A$

$= 4 \times A$

$= 7 \times A$

Indices correspond to
$(h^2+hk+k^2) = 1, 3, 4, 7,….$ or
$hk = 10, 11, 20, 21$

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Already calculated the sin square θ value, and then divided each sin square θ value by integers like 3,4,7 because that is the normal crystals structure for the hexagonal that tetragonal one, so from h square plus h k plus k square allowed by the structure factor. Then look for the lowest common quotient, so from these we are going to get the lowest common quotients and then the lowest common quotients is A, which is nothing but the 0.0908, so in this particular case we are getting the common lowest value is this one and then peeks with the lowest common quotients are h k zero type peaks.

Assign allowed h k zero indices to the peaks itself. So now after that what we are going to do? We are going to do indices correspondent to a square plus h k plus k square is equal to 1,3,4,7 or maybe h k is equal to 10, 11, 20, or maybe the 21. So that means h k is equal to 101120 and 21.

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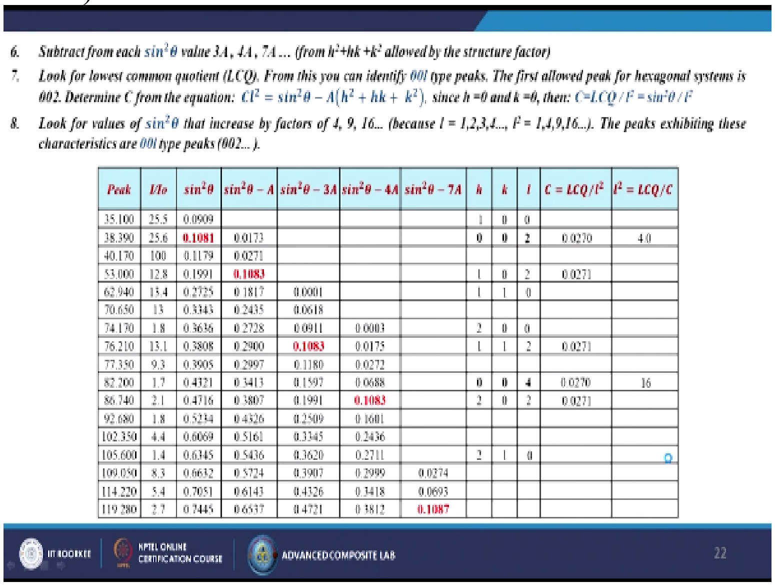

6. *Subtract from each $\sin^2\theta$ value 3A, 4A, 7A ... (from h^2+hk+k^2 allowed by the structure factor)*
7. *Look for lowest common quotient (LCQ). From this you can identify 00l type peaks. The first allowed peak for hexagonal systems is 002. Determine C from the equation: $Cl^2 = \sin^2\theta - A(h^2 + hk + k^2)$, since h =0 and k =0, then: $C = LCQ / l^2 = \sin^2\theta / l^2$*
8. *Look for values of $\sin^2\theta$ that increase by factors of 4, 9, 16... (because l = 1,2,3,4..., l^2 = 1,4,9,16...). The peaks exhibiting these characteristics are 00l type peaks (002...).*

Peak	I/Io	$\sin^2\theta$	$\sin^2\theta - A$	$\sin^2\theta - 3A$	$\sin^2\theta - 4A$	$\sin^2\theta - 7A$	h	k	l	$C = LCQ/l^2$	$l^2 = LCQ/C$
35.100	25.5	0.0909					1	0	0		
38.390	25.6	**0.1081**	0.0173				**0**	**0**	**2**	0.0270	4.0
40.170	100	0.1179	0.0271								
53.000	12.8	0.1991	**0.1083**				1	0	2	0.0271	
62.940	13.4	0.2725	0.1817	0.0001			1	1	0		
70.650	13	0.3343	0.2435	0.0618							
74.170	1.8	0.3636	0.2728	0.0911	0.0003		2	0	0		
76.210	13.1	0.3808	0.2900	**0.1083**	0.0175		1	1	2	0.0271	
77.350	9.3	0.3905	0.2997	0.1180	0.0272						
82.200	1.7	0.4321	0.3413	0.1597	0.0688		**0**	**0**	**4**	0.0270	16
86.740	2.1	0.4716	0.3807	0.1991	**0.1083**		2	0	2	0.0271	
92.680	1.8	0.5234	0.4326	0.2509	0.1601						
102.350	4.4	0.6069	0.5161	0.3345	0.2436						
105.600	1.4	0.6345	0.5436	0.3620	0.2711		2	1	0		
109.050	8.3	0.6632	0.5724	0.3907	0.2999	0.0274					
114.220	5.4	0.7051	0.6143	0.4326	0.3418	0.0693					
119.280	2.7	0.7445	0.6537	0.4721	0.3812	**0.1087**					

Then what we are going to do? We are going to subtract from each sin square θ value from 3a, 4a, 7a, from h square plus hk plus k square allowed by the structure factor, look for the lowest common quotient from these, you can identify 001 type peaks, the first allowed peaks for the hexagonal system is 002 to determine the c from the equations, if we follow the equations like c l square is equal to sin square θ minus A into A square plus hk plus k square.

Since h zero and k zero then c is equal to l c cube by l square which is nothing but sin square θ by l square, so from this particular case we are getting that each case, suppose if I give the examples in this particular case we are getting the each k l value is 002, and if I put the l value over here then easily we can calculate the c and if I get the c then we can get the l square value, which is nothing but 4 in this particular case.

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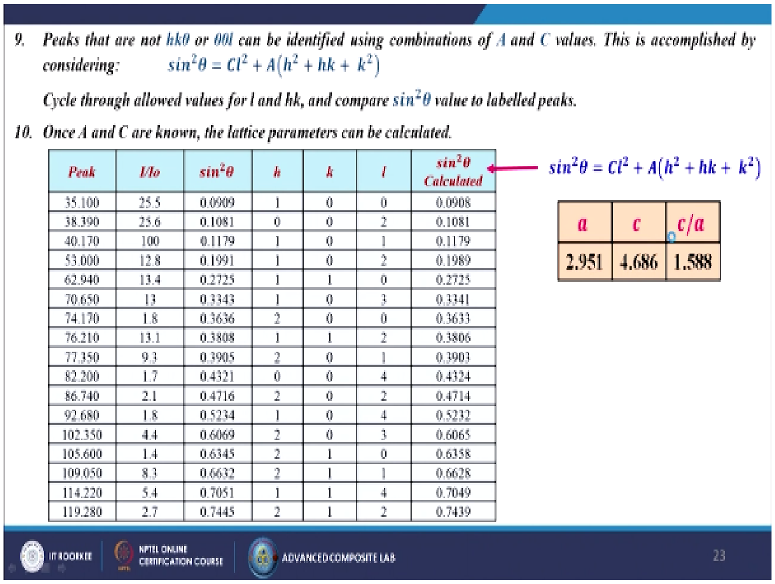

9. *Peaks that are not hk0 or 00l can be identified using combinations of A and C values. This is accomplished by considering:* $\sin^2\theta = Cl^2 + A(h^2 + hk + k^2)$

Cycle through allowed values for l and hk, and compare $\sin^2\theta$ *value to labelled peaks.*

10. *Once A and C are known, the lattice parameters can be calculated.*

Peak	I/Io	$\sin^2\theta$	h	k	l	$\sin^2\theta$ Calculated
35.100	25.5	0.0909	1	0	0	0.0908
38.390	25.6	0.1081	0	0	2	0.1081
40.170	100	0.1179	1	0	1	0.1179
53.000	12.8	0.1991	1	0	2	0.1989
62.940	13.4	0.2725	1	1	0	0.2725
70.650	13	0.3343	1	0	3	0.3341
74.170	1.8	0.3636	2	0	0	0.3633
76.210	13.1	0.3808	1	1	2	0.3806
77.350	9.3	0.3905	2	0	1	0.3903
82.200	1.7	0.4321	0	0	4	0.4324
86.740	2.1	0.4716	2	0	2	0.4714
92.680	1.8	0.5234	1	0	4	0.5232
102.350	4.4	0.6069	2	0	3	0.6065
105.600	1.4	0.6345	2	1	0	0.6358
109.050	8.3	0.6632	2	1	1	0.6628
114.220	5.4	0.7051	1	1	4	0.7049
119.280	2.7	0.7445	2	1	2	0.7439

$\sin^2\theta = Cl^2 + A(h^2 + hk + k^2)$

a	c	c/a
2.951	4.686	1.588

So in this particular slide, so peaks are that are not h k zero or 00L can be identify the using combinations of A and C values, these is atom pleased by the considering sin square θ is equal to c l square plus A into A square plus hk plus k square. So in this particular slide you can get, that sin square θ value we have obtained ion this one and this is the sin square θ value calculated. And that is more or less matching with the sin square θ value obtained, by using this equation and from this particular table we can easily calculate the value of A C and C by A ratio.

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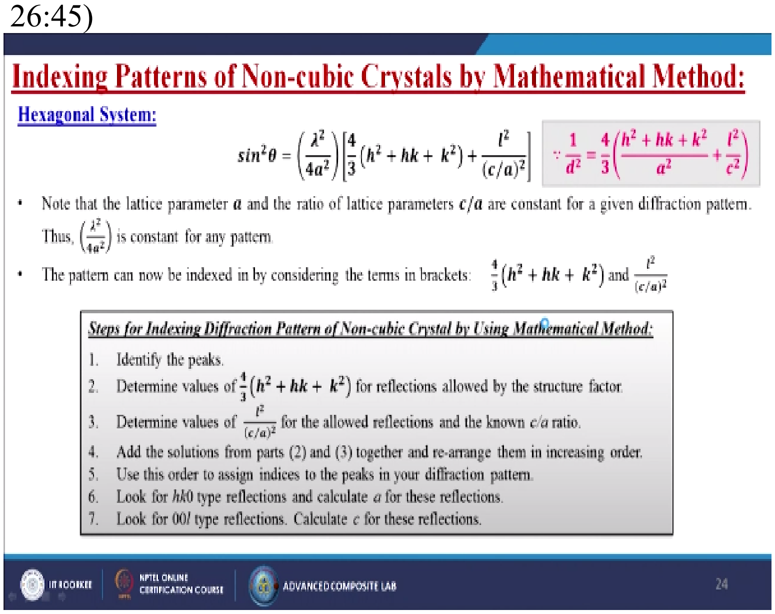

Indexing Patterns of Non-cubic Crystals by Mathematical Method:

Hexagonal System:

$$\sin^2\theta = \left(\frac{\lambda^2}{4a^2}\right)\left[\frac{4}{3}(h^2 + hk + k^2) + \frac{l^2}{(c/a)^2}\right] \quad \because \frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2}\right)$$

- Note that the lattice parameter a and the ratio of lattice parameters c/a are constant for a given diffraction pattern. Thus, $\left(\frac{\lambda^2}{4a^2}\right)$ is constant for any pattern.
- The pattern can now be indexed in by considering the terms in brackets: $\frac{4}{3}(h^2 + hk + k^2)$ and $\frac{l^2}{(c/a)^2}$

Steps for Indexing Diffraction Pattern of Non-cubic Crystal by Using Mathematical Method:

1. Identify the peaks.
2. Determine values of $\frac{4}{3}(h^2 + hk + k^2)$ for reflections allowed by the structure factor.
3. Determine values of $\frac{l^2}{(c/a)^2}$ for the allowed reflections and the known c/a ratio.
4. Add the solutions from parts (2) and (3) together and re-arrange them in increasing order.
5. Use this order to assign indices to the peaks in your diffraction pattern.
6. Look for *hk*0 type reflections and calculate *a* for these reflections.
7. Look for 00*l* type reflections. Calculate *c* for these reflections.

And then we are going to discuss about the indexing pattern of non cubic crystals by mathematical method, So for the hexagonal systems, we know sin square θ is equal to λ square by 4a square into 4 by 3 A square plus h k plus k square plus l square by c by A whole square. So also in note of for the hexagonal systems one by d square is equal to 4 by 3 into h square plus h k plus k square by A square plus l square by C square. So in this particular case they are two terms, so we are denoting it as a, A and C by A, so in this particular case so the pattern now being indexed by considering the terms in brackets like 4 by 3 A square plus h k plus k square and another term is l square plus C by A whole square, so this is number one and this is number two. So first what we have to do?

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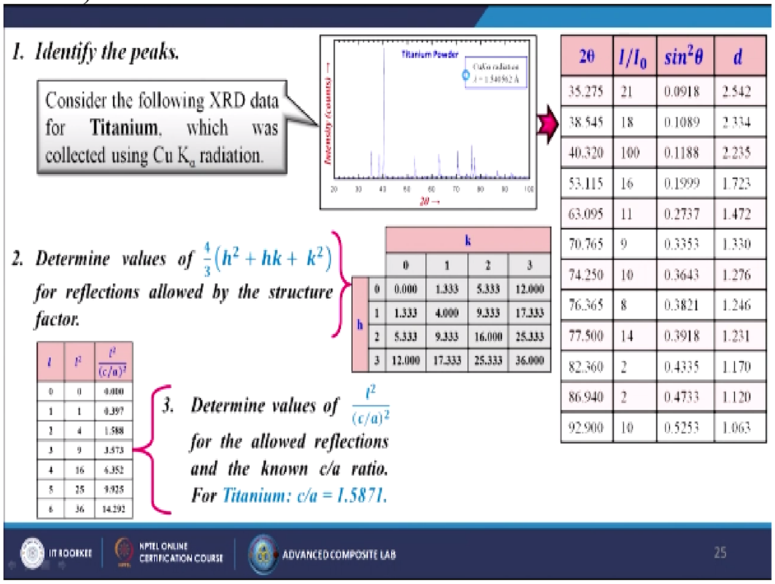

1. *Identify the peaks.*

Consider the following XRD data for **Titanium**, which was collected using Cu K_α radiation.

2θ	I/I_0	$\sin^2\theta$	d
35.275	21	0.0918	2.542
38.545	18	0.1089	2.334
40.320	100	0.1188	2.235
53.115	16	0.1999	1.723
63.095	11	0.2737	1.472
70.765	9	0.3353	1.330
74.250	10	0.3643	1.276
76.365	8	0.3821	1.246
77.500	14	0.3918	1.231
82.360	2	0.4335	1.170
86.940	2	0.4733	1.120
92.900	10	0.5253	1.063

2. *Determine values of* $\frac{4}{3}(h^2 + hk + k^2)$ *for reflections allowed by the structure factor.*

		k			
		0	1	2	3
h	0	0.000	1.333	5.333	12.000
	1	1.333	4.000	9.333	17.333
	2	5.333	9.333	16.000	25.333
	3	12.000	17.333	25.333	36.000

3. *Determine values of* $\frac{l^2}{(c/a)^2}$ *for the allowed reflections and the known c/a ratio. For Titanium: c/a = 1.5871.*

l	l^2	$\frac{l^2}{(c/a)^2}$
0	0	0.000
1	1	0.397
2	4	1.588
3	9	3.573
4	16	6.352
5	25	9.925
6	36	14.292

In the next slides, say suppose I am giving a examples of the titanium powder in that titanium powder we are getting the peaks over there, and then from that we are getting the two θ value. And we are getting the value of I by I zero, then we are making sin square θ value or maybe we are getting the sin square θ value from this particular case.

Now we are having two parameters already I have mentioned number one and number two, so first we are going to calculate the 4 by 3 into h square plus h k plus k square value. In this particular case a leads absolutely zero and then we are putting h values once zero k value zero, h value zero k value one, h value 1, k value 2, h value zero, k value 3, like this way we are getting this particular table and then in the second conditions we are determine the value of l square by c by A whole square.

In this case we are assuming that h and h k value all are the zero. And from these particular case we are getting the value of l, we are getting the value of l square and l square by c by A whole square value.

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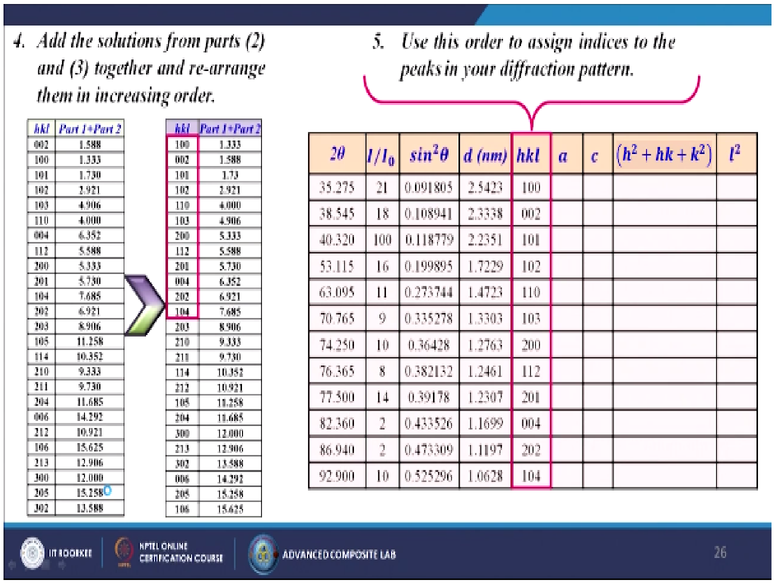

4. *Add the solutions from parts (2) and (3) together and re-arrange them in increasing order.*

hkl	Part 1+Part 2
002	1.588
100	1.333
101	1.730
102	2.921
103	4.906
110	4.000
004	6.352
112	5.588
200	5.333
201	5.730
104	7.685
202	6.921
203	8.906
105	11.258
114	10.352
210	9.333
211	9.730
204	11.685
006	14.292
212	10.921
106	15.625
213	12.906
300	12.000
205	15.258
302	13.588

hkl	Part 1+Part 2
100	1.333
002	1.588
101	1.73
102	2.921
110	4.000
103	4.906
200	5.333
112	5.588
201	5.730
004	6.352
202	6.921
104	7.685
203	8.906
210	9.333
211	9.730
114	10.352
212	10.921
105	11.258
204	11.685
300	12.000
213	12.906
302	13.588
006	14.292
205	15.258
106	15.625

5. *Use this order to assign indices to the peaks in your diffraction pattern.*

2θ	I/I_0	$sin^2\theta$	d (nm)	hkl	a	c	(h^2+hk+k^2)	l^2
35.275	21	0.091805	2.5423	100				
38.545	18	0.108941	2.3338	002				
40.320	100	0.118779	2.2351	101				
53.115	16	0.199895	1.7229	102				
63.095	11	0.273744	1.4723	110				
70.765	9	0.335278	1.3303	103				
74.250	10	0.36428	1.2763	200				
76.365	8	0.382132	1.2461	112				
77.500	14	0.39178	1.2307	201				
82.360	2	0.433526	1.1699	004				
86.940	2	0.473309	1.1197	202				
92.900	10	0.525296	1.0628	104				

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And then after that we are adding the part1 means number one equations with the number two equations and then with the correspondence h k l value we are adding those two parameters. And then after that just we are arranging these value from the increasing order and then from these particular value because it is that hexagonal in shape, so that is why 001 is not possible so that's why you are starting the value from calculating from 002.

And then we are calculating the values and then that top of total 12 values because, as per the hexagonal peaks that 1, 3,4,6,7 like that we are taking all those number of values and then we are putting in these from where we are calculating the d and h k l and you have already calculated that A C plus A square plus k square plus l square and l square value.

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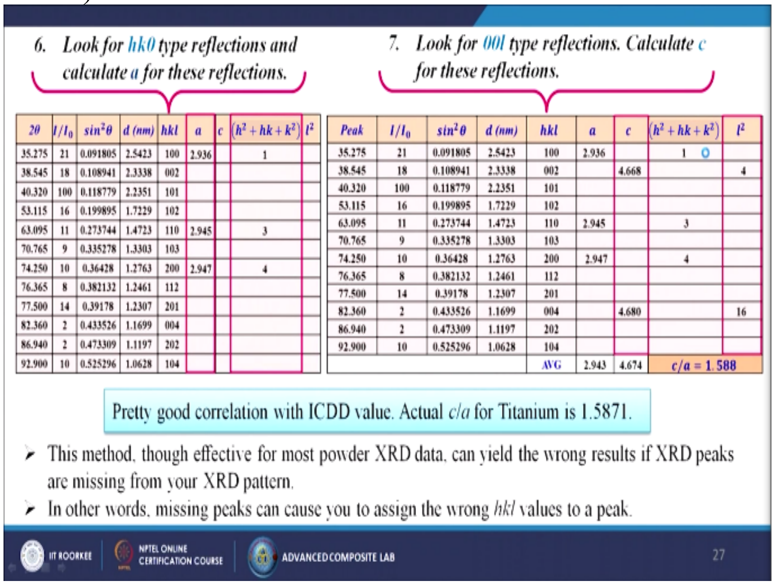

6. *Look for hk0 type reflections and calculate a for these reflections.*

2θ	I/I_0	$sin^2\theta$	d (nm)	hkl	a	c	(h^2+hk+k^2)	l^2
35.275	21	0.091805	2.5423	100	2.936		1	
38.545	18	0.108941	2.3338	002				
40.320	100	0.118779	2.2351	101				
53.115	16	0.199895	1.7229	102				
63.095	11	0.273744	1.4723	110	2.945		3	
70.765	9	0.335278	1.3303	103				
74.250	10	0.36428	1.2763	200	2.947		4	
76.365	8	0.382132	1.2461	112				
77.500	14	0.39178	1.2307	201				
82.360	2	0.433526	1.1699	004				
86.940	2	0.473309	1.1197	202				
92.900	10	0.525296	1.0628	104				

7. *Look for 00l type reflections. Calculate c for these reflections.*

Peak	I/I_0	$sin^2\theta$	d (nm)	hkl	a	c	(h^2+hk+k^2)	l^2
35.275	21	0.091805	2.5423	100	2.936		1	
38.545	18	0.108941	2.3338	002		4.668		4
40.320	100	0.118779	2.2351	101				
53.115	16	0.199895	1.7229	102				
63.095	11	0.273744	1.4723	110	2.945		3	
70.765	9	0.335278	1.3303	103				
74.250	10	0.36428	1.2763	200	2.947		4	
76.365	8	0.382132	1.2461	112				
77.500	14	0.39178	1.2307	201				
82.360	2	0.433526	1.1699	004		4.680		16
86.940	2	0.473309	1.1197	202				
92.900	10	0.525296	1.0628	104				
				AVG	2.943	4.674	c/a = 1.588	

Pretty good correlation with ICDD value. Actual *c/a* for Titanium is 1.5871.

- This method, though effective for most powder XRD data, can yield the wrong results if XRD peaks are missing from your XRD pattern.
- In other words, missing peaks can cause you to assign the wrong *hkl* values to a peak.

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And then this particular case look for the h k zero type reflections and calculate A for this kind of reflections, so here h k l value you know? So from there we can calculate the A value in this particular case. As the h k l is 100 so automatically the A square plus k square plus l square is one and if we see that, this is for the 200 that means A square plus k square plus l square is 4 and we are getting the A value is 2.947, and from these after that look for 001 type reflection calculate the c for this reflections.

Now we are calculating the c value in this particular position, and then from that we are putting l square value of that particular against that particular peak. So here pretty good correlation with ICDD value, this is a one kind of database actual c by A for titanium is 1.5871 and here why we are doing average of A value, we are getting that average value of A is 2.943, and for average of c is 4.674, and the c by A ratio is 1.588.

And the actual value which is already in the ICDD value is 1.5871. So that means, it is more or less or maybe same like our actual calculated value and with the ICDD value. So these methods affective for most powdered XRD data and can yield the wrong result if XRD peaks are missing from your XRD pattern. In the other words, missing peaks can cause you to assign the wrong hkl values to peak.

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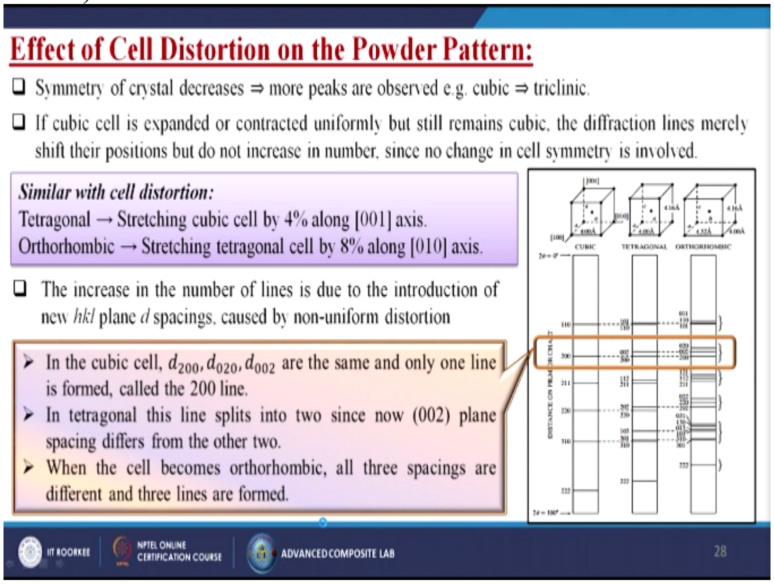

Effect of Cell Distortion on the Powder Pattern:

- ❑ Symmetry of crystal decreases ⇒ more peaks are observed e.g. cubic ⇒ triclinic.
- ❑ If cubic cell is expanded or contracted uniformly but still remains cubic, the diffraction lines merely shift their positions but do not increase in number, since no change in cell symmetry is involved.

Similar with cell distortion:
Tetragonal → Stretching cubic cell by 4% along [001] axis.
Orthorhombic → Stretching tetragonal cell by 8% along [010] axis.

- ❑ The increase in the number of lines is due to the introduction of new *hkl* plane *d* spacings, caused by non-uniform distortion

- ➢ In the cubic cell, $d_{200}, d_{020}, d_{002}$ are the same and only one line is formed, called the 200 line.
- ➢ In tetragonal this line splits into two since now (002) plane spacing differs from the other two.
- ➢ When the cell becomes orthorhombic, all three spacings are different and three lines are formed.

Now we are going to discuss about the effect of cell distortion on the powder pattern: so the symmetry of crystal decreases more peaks are observed, that means cubic correspondent to the triclinic. If cubic cell is expanded or contracted uniformly, but still remains cubic, the diffraction lines mercly shift their position but do not increase in number, since no change in cell symmetry is involved.

So similar with the cell distortion what happens, for tetragonal, stretching cubic cell by 4% along 001 axis, for orthorhombic, stretching tetragonal cell by 8% along 010 axis. So in this particular case we are giving the examples, in the cubic cell d200, d020, and d002 are the same and only one line is formed, called the 200 line. So this is actually the 200 line has been formed. In tetragonal this line splits in two since now 002 plane spacing differs from the other 21. So in this particular case we are getting the different lines for each different peak, when the cell becomes orthorhombic, all three spacing's are different and three lines are formed.

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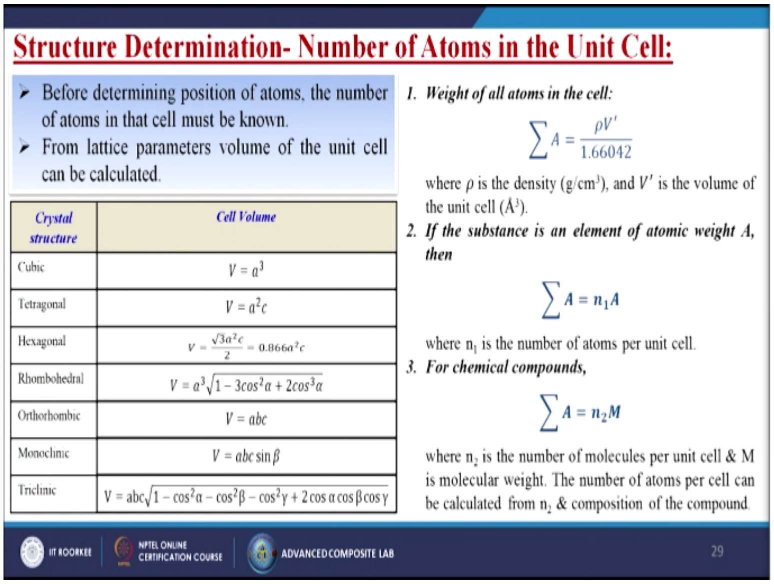

Structure Determination- Number of Atoms in the Unit Cell:

- Before determining position of atoms, the number of atoms in that cell must be known.
- From lattice parameters volume of the unit cell can be calculated.

Crystal structure	*Cell Volume*
Cubic	$V = a^3$
Tetragonal	$V = a^2c$
Hexagonal	$V = \frac{\sqrt{3}a^2c}{2} = 0.866a^2c$
Rhombohedral	$V = a^3\sqrt{1 - 3\cos^2\alpha + 2\cos^3\alpha}$
Orthorhombic	$V = abc$
Monoclinic	$V = abc\sin\beta$
Triclinic	$V = abc\sqrt{1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma}$

1. ***Weight of all atoms in the cell:***

$$\sum A = \frac{\rho V'}{1.66042}$$

where ρ is the density (g/cm^3), and V' is the volume of the unit cell (Å^3).

2. ***If the substance is an element of atomic weight A, then***

$$\sum A = n_1 A$$

where n_1 is the number of atoms per unit cell.

3. ***For chemical compounds,***

$$\sum A = n_2 M$$

where n_2 is the number of molecules per unit cell & M is molecular weight. The number of atoms per cell can be calculated from n_2 & composition of the compound.

So in this particular slide we are going to discuss about the structure determination number of atoms in the unit cell: so in this case first we are going to discuss about the cubic generally the cell volume is capital V is equal to A, cube. For tetragonal it is v is equal to A square c, so like this way we can calculate the cell volume for cubic tetragonal, hexagonal, rhombohedra, orthorhombic and for the tri clinic also.

From this particular case we can make sure weight of all atoms in the cells also, so like this way summation over A is equal to row weight prime by 1.66042. Where row is the density which is gram per cm cube and v prime is the volume of a unit cell that is angstrom cube. If the substance is the element of atomic weight A, then summation over A is equal to n1 A, where n1 is the number of atoms per unit cell.

For chemical compounds, summation over A is equal to n2 into capital M. where n2 is the number of molecules per unit cell & m is the molecular weight of that particular material. So the number of atoms per cell can be calculated from n2 & composition of the compound itself.

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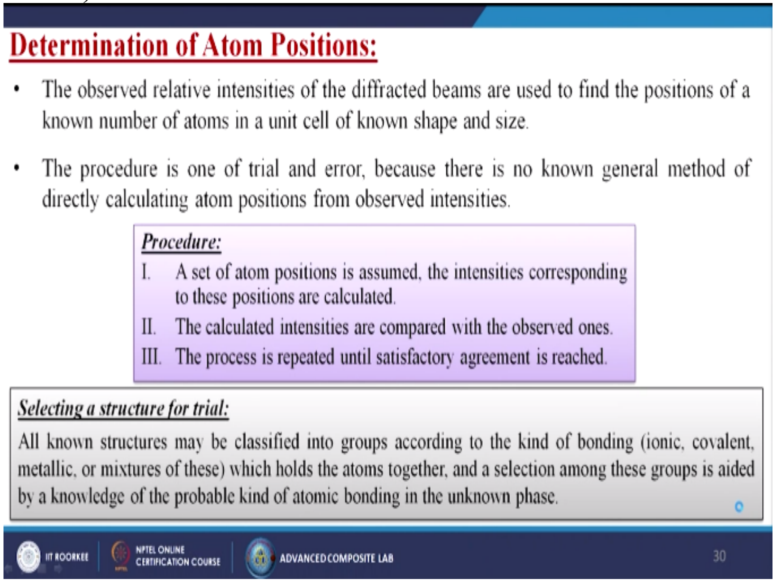

Determination of Atom Positions:

- The observed relative intensities of the diffracted beams are used to find the positions of a known number of atoms in a unit cell of known shape and size.
- The procedure is one of trial and error, because there is no known general method of directly calculating atom positions from observed intensities.

Procedure:

I. A set of atom positions is assumed, the intensities corresponding to these positions are calculated.

II. The calculated intensities are compared with the observed ones.

III. The process is repeated until satisfactory agreement is reached.

Selecting a structure for trial:

All known structures may be classified into groups according to the kind of bonding (ionic, covalent, metallic, or mixtures of these) which holds the atoms together, and a selection among these groups is aided by a knowledge of the probable kind of atomic bonding in the unknown phase.

Now we are going to discuss about the determination of atom positions: so the observed relative intensities of the diffracted beams are used to find the position of a known number of atoms in a unit cell of known shape and size. The procedure is one of trial and error, because there is no known general method of directly calculating atoms position from observed intensities. What are the procedures?

Number one is that, a set of atoms position is assumed; the intensities corresponding to these positions are calculated. Then number two, the calculated intensities are compared with the observed ones. And the third is the process is repeated until satisfactory agreement is reached, so how to select a structure for trial?

All known structures may be classified into groups according to the kind of bonding like ionic bonding, covalent bonding, metallic bonding, or maybe the mixture of these, which holds the atoms together, and a selection among these groups is aided by knowledge of the probable kind of atomic bonding in the unknown phase.

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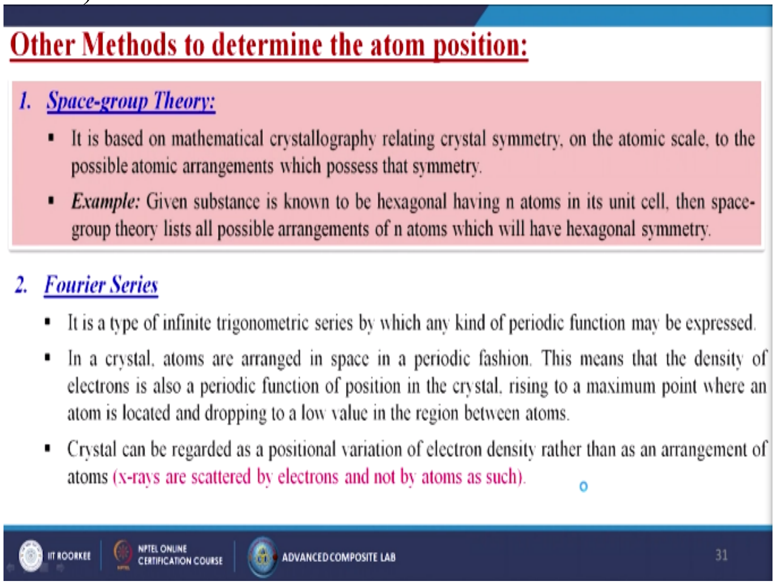

Other Methods to determine the atom position:

1. ***Space-group Theory:***
   - It is based on mathematical crystallography relating crystal symmetry, on the atomic scale, to the possible atomic arrangements which possess that symmetry.
   - ***Example:*** Given substance is known to be hexagonal having n atoms in its unit cell, then space-group theory lists all possible arrangements of n atoms which will have hexagonal symmetry.
2. ***Fourier Series***
   - It is a type of infinite trigonometric series by which any kind of periodic function may be expressed.
   - In a crystal, atoms are arranged in space in a periodic fashion. This means that the density of electrons is also a periodic function of position in the crystal, rising to a maximum point where an atom is located and dropping to a low value in the region between atoms.
   - Crystal can be regarded as a positional variation of electron density rather than as an arrangement of atoms (x-rays are scattered by electrons and not by atoms as such).

There are some other method to determine the atom positions also, first one is called the space group theory, it is based on mathematical crystallography relating crystals symmetry, on the atomic scale, to the possible atomic arrangements which posses the symmetry. Example, given substances is known to be hexagonal having n atoms in its unit cell, then space group theory list all possible arrangement of n atom which will have hexagonal symmetry.

So it is one kind of mismatch kind of things. Then the second one is that Fourier series, it is a type of infinite trigonometric series by which any kind of periodic function may be expressed. In a crystal, atoms are arranged in space in a periodic fashion. This means that means that the density of electron is also a periodic function of position in the crystal.

Rising to a maximum point where an atom is located and dropping to a low value in the region between atoms. Crystal can be regarded as a positional variation of electron density rather than as an arrangement of atoms, x-ray are scattered by electron and not by atoms as such.

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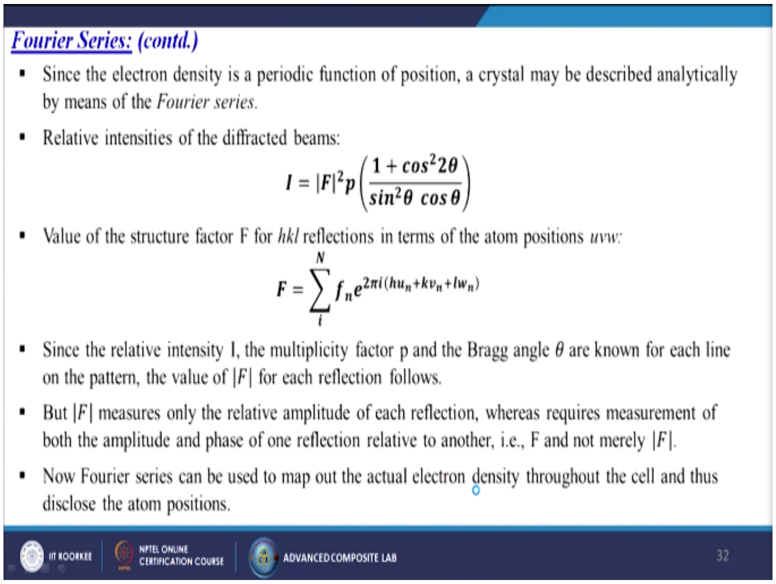

Fourier Series: (contd.)

- Since the electron density is a periodic function of position, a crystal may be described analytically by means of the *Fourier series.*
- Relative intensities of the diffracted beams:

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

- Value of the structure factor F for *hkl* reflections in terms of the atom positions *uvw:*

$$F = \sum_{i}^{N} f_n e^{2\pi i(hu_n+kv_n+lw_n)}$$

- Since the relative intensity I, the multiplicity factor p and the Bragg angle θ are known for each line on the pattern, the value of $|F|$ for each reflection follows.
- But $|F|$ measures only the relative amplitude of each reflection, whereas requires measurement of both the amplitude and phase of one reflection relative to another, i.e., F and not merely $|F|$.
- Now Fourier series can be used to map out the actual electron density throughout the cell and thus disclose the atom positions.

So what is the Fourier series: since the electron density is a periodic function of position, a crystal may be described analytically by means of the Fourier series? So relative intensities of the diffracted beams I is equal to function f square into p multiplied by one plus cos square 2 θ by sin square θ cos θ, value of the structure factor f because here the f is known as the structure factor.

So already we have gone through in our previous slides, so here the structure factor F for each reflection in terms of the atom positions UVW is f is equal to summation over, I to capital N, if n e to the power two pie I into each UN plus KVN plus LWN. Since the relative intensity I, the multiplicity factor p and the Bragg angle θ are known for each line on the pattern, and then the structure factor for each reflection follows.

But structure factor measure only the relative amplitude of each reflection, whereas requires measurement both the amplitude and phase of one reflection relative to another. F and not merely the F magnitude of F. So now Fourier series can be used to map out the actual electron density throughout the cell and thus disclose the atom positions.

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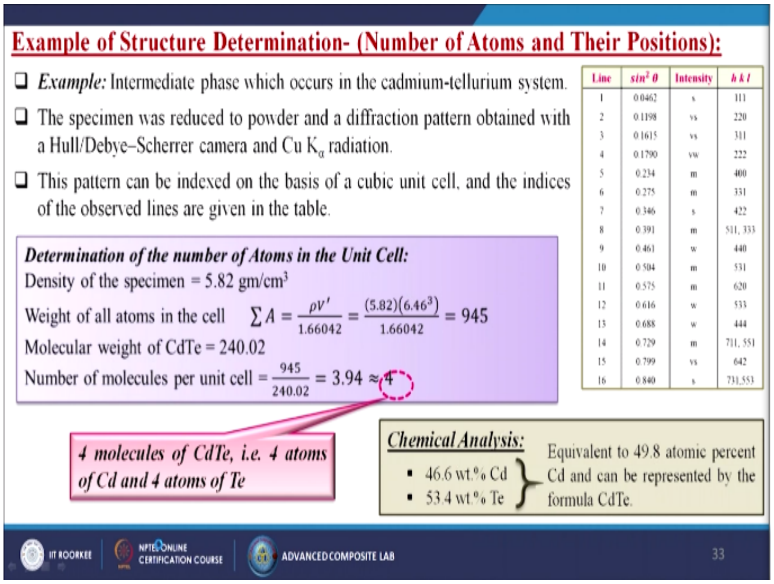

Example of Structure Determination- (Number of Atoms and Their Positions):

- ☐ *Example:* Intermediate phase which occurs in the cadmium-tellurium system.
- ☐ The specimen was reduced to powder and a diffraction pattern obtained with a Hull/Debye–Scherrer camera and Cu K_α radiation.
- ☐ This pattern can be indexed on the basis of a cubic unit cell, and the indices of the observed lines are given in the table.

Line	$sin^2\theta$	Intensity	hkl
1	0.0462	s	111
2	0.1198	vs	220
3	0.1615	vs	311
4	0.1790	vw	222
5	0.234	m	400
6	0.275	m	331
7	0.346	s	422
8	0.391	m	511, 333
9	0.461	w	440
10	0.504	m	531
11	0.575	m	620
12	0.616	w	533
13	0.688	w	444
14	0.729	m	711, 551
15	0.799	vs	642
16	0.840	s	731,553

Determination of the number of Atoms in the Unit Cell:

Density of the specimen = 5.82 gm/cm^3

Weight of all atoms in the cell $\sum A = \frac{\rho V'}{1.66042} = \frac{(5.82)(6.46^3)}{1.66042} = 945$

Molecular weight of CdTe = 240.02

Number of molecules per unit cell $= \frac{945}{240.02} = 3.94 \approx 4$

4 molecules of CdTe, i.e. 4 atoms of Cd and 4 atoms of Te

Chemical Analysis:

- 46.6 wt.% Cd
- 53.4 wt.% Te

Equivalent to 49.8 atomic percent Cd and can be represented by the formula CdTe.

So now we are going to an example of structure determinations number of atoms and their positions. So example, like an intermediate phase which occurs in the cadmium-tellurium systems CDTE, the specimen was reduced to powder and a diffraction pattern obtained with a Hull/Debye-Scherrer camera and copper k α radiations.

This pattern can be indexed on the basic of a cubic unit cell, and the indices of the observed lines are given in the table. So from these particular case we have received the two θ value from there we can have calculated the sin square θ, then intensity and the hkl value. Then determination of the number of atoms in the unit cell, density of the specimen is 5.82 gm per cm cube.

Weight of all atoms in the cell summation over A is equal to row v prime by 1.66042, which is nothing but the 5.82 into 6.46 cubes by 1.66042 which is nothing but the 945. So molecular weight of cadmium tellurium is 240.02, number of molecules per unit cell means 945 by 240.02, which is nothing but is equal to 3.94 more or less, is equal to 4, so 4 molecules of CdTe, that means four atoms of cadmium and four atoms of tellurium is present. And what is the chemical analysis? So generally 46.6 is the weight percent of cadmium and 53.4 weight percent of tellurium equivalent to 49.8 atomic percent of Cd can be represented by the formula like cadmium tellurium.

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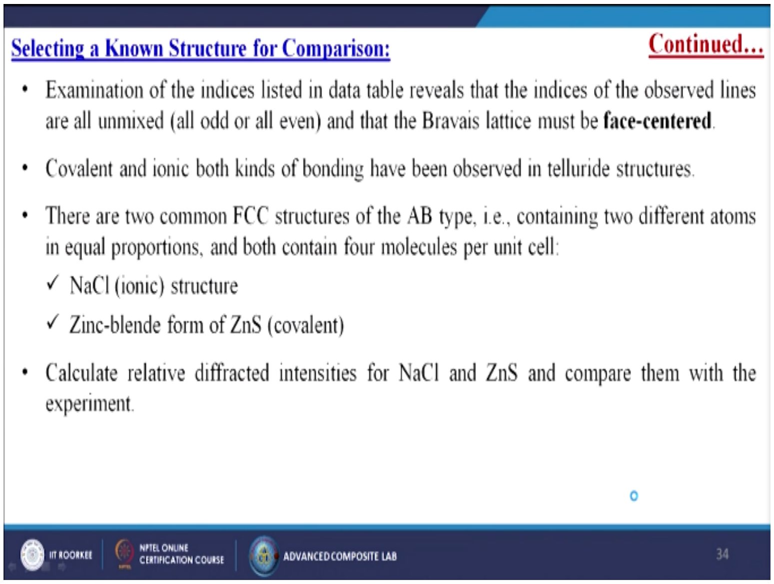

Selecting a Known Structure for Comparison: **Continued…**

- Examination of the indices listed in data table reveals that the indices of the observed lines are all unmixed (all odd or all even) and that the Bravais lattice must be **face-centered**.
- Covalent and ionic both kinds of bonding have been observed in telluride structures.
- There are two common FCC structures of the AB type, i.e., containing two different atoms in equal proportions, and both contain four molecules per unit cell:
  - ✓ NaCl (ionic) structure
  - ✓ Zinc-blende form of ZnS (covalent)
- Calculate relative diffracted intensities for NaCl and ZnS and compare them with the experiment.

So if we are having a known structure for selecting a known structure for comparison, examination of the indices listed in data table reveals that that the indices of the observed lines are all unmixed, all odd or maybe all even, and that the Bravais lattice must be face centered. Covalent and ionic both kind of bonding have been observed in telluride structures.

There are two common FCC structures of the AB type, that means containing two different atoms in equal proportion, and both contain four molecules per unit cells, sodium chloride ionic structure, zinc-blende form zinc sulphide which is covalent in nature. Calculate the relative diffracted intensities for sodium chloride and zinc sulphide and compare them with the experiment.

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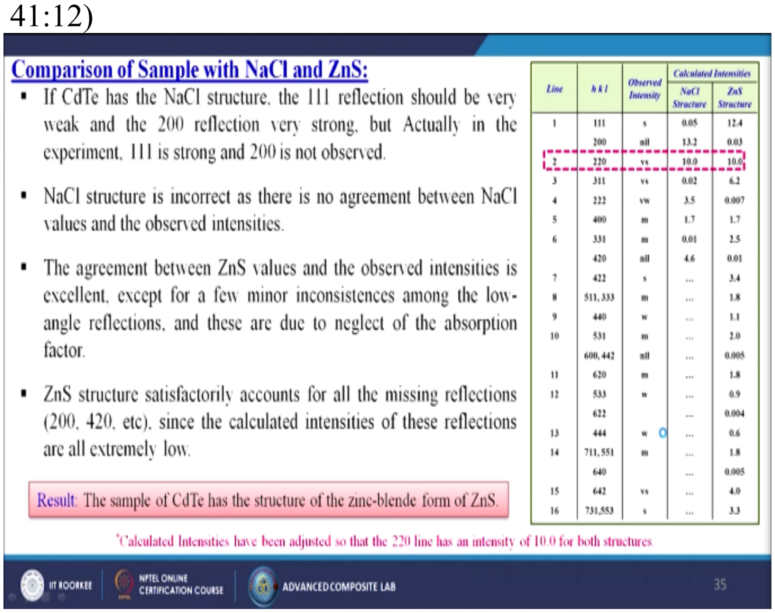

Comparison of Sample with NaCl and ZnS:

- If CdTe has the NaCl structure, the 111 reflection should be very weak and the 200 reflection very strong, but Actually in the experiment, 111 is strong and 200 is not observed.
- NaCl structure is incorrect as there is no agreement between NaCl values and the observed intensities.
- The agreement between ZnS values and the observed intensities is excellent, except for a few minor inconsistences among the low-angle reflections, and these are due to neglect of the absorption factor.
- ZnS structure satisfactorily accounts for all the missing reflections (200, 420, etc), since the calculated intensities of these reflections are all extremely low.

Result: The sample of CdTe has the structure of the zinc-blende form of ZnS.

Line	h k l	Observed Intensity	Calculated Intensities	
			NaCl Structure	ZnS Structure
1	111	s	0.05	12.4
	200	nil	13.2	0.03
2	220	vs	10.0	10.0
3	311	vs	0.02	6.2
4	222	vw	3.5	0.007
5	400	m	1.7	1.7
6	331	m	0.01	2.5
	420	nil	4.6	0.01
7	422	s	...	3.4
8	511, 333	m	...	1.8
9	440	w	...	1.1
10	531	m	...	2.0
	600, 442	nil	...	0.005
11	620	m	...	1.8
12	533	w	...	0.9
	622		...	0.004
13	444	w	...	0.6
14	711, 551	m	...	1.8
	640		...	0.005
15	642	vs	...	4.0
16	731,553	s	...	3.3

*Calculated Intensities have been adjusted so that the 220 line has an intensity of 10.0 for both structures.

So now we are going to do the comparison of sample with the sodium chloride and zinc sulphide. So if that cadmium, tellurium has the NaCl structure, the 111 reflection should be very weak and the 200 reflection very strong. But actually in the experiment 111 is strong and 200 is not observed, so it is almost the opposite. Sodium chloride structure is incorrect as there is no agreement between sodium chloride value and the observed intensities.

The agreement between zinc sulphide values and the observed intensities is excellent, except for a few minor inconsistencies among the low angle reflections, and these are due to neglect of the absorption factor. Zinc sulphide structure satisfactorily accounts for all missing reflections like, 200,420 etc. since the calculated intensities of these reflections are all extremely low. So in this case we are getting that 200 value here hkl value 200, then sodium chloride structure that calculated intensities are coming 10 and for zinc sulphide also the calculated intensities are coming 10.

So that is matching with the sodium chloride and the zinc sulphide. So result the sample of CdTe has the structure of the zinc-blende form of zinc sulphide because it is matching with this zinc sulphide. So from this particular lecture we have got some basic principles of structure determinations,

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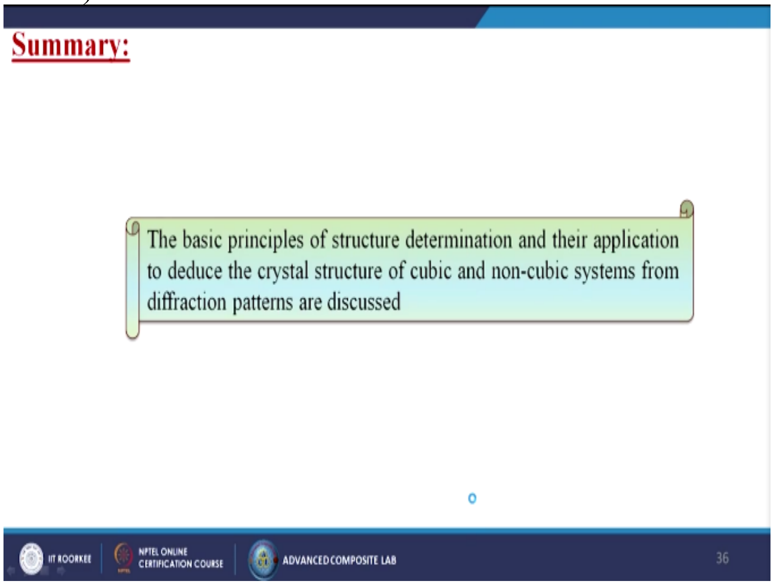

Summary:

The basic principles of structure determination and their application to deduce the crystal structure of cubic and non-cubic systems from diffraction patterns are discussed

And their application to deduce the crystal structure of cubic and non cubic systems from diffraction pattern which we have discussed in this particular lecture thank you.

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