Chemical Crystallography
Prof. Angshuman Roy Choudhury
Department of Chemical Sciences
Indian Institution of Science Education and Research, Mohali

Basics, Symmetry and Equivalent Points in Crystallography
Lecture - 02
Sources of X-Rays, Crystal Systems and Bravais lattices

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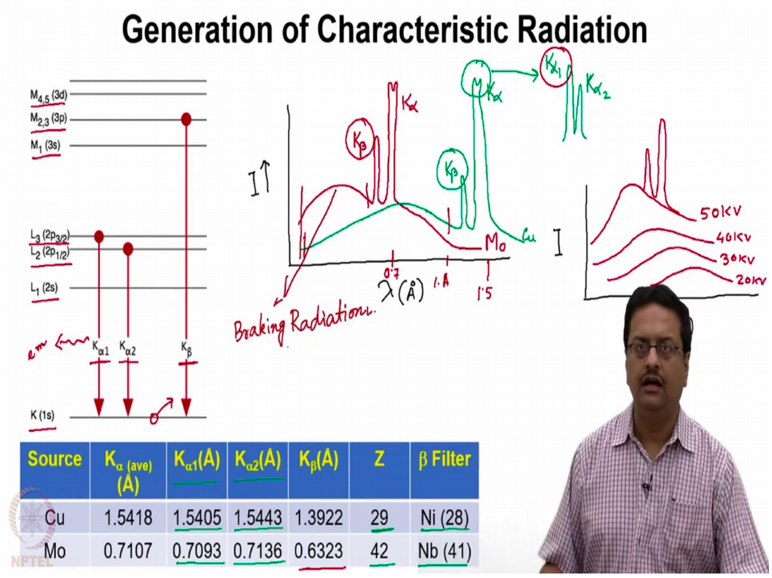

Generation of Characteristic Radiation

Source	$K_{\alpha\,(ave)}$ (Å)	$K_{\alpha1}$(Å)	$K_{\alpha2}$(Å)	K_β(Å)	Z	β Filter
Cu	1.5418	1.5405	1.5443	1.3922	29	Ni (28)
Mo	0.7107	0.7093	0.7136	0.6323	42	Nb (41)

Welcome back to the 2nd lecture of this course on Chemical Crystallography. I am starting this lecture from the slide that where we ended the previous lecture where we discussed how the generation of characteristic radiation is done, and how those radiations can be used for our experiments in the laboratory, we using appropriate filter and monochromator.

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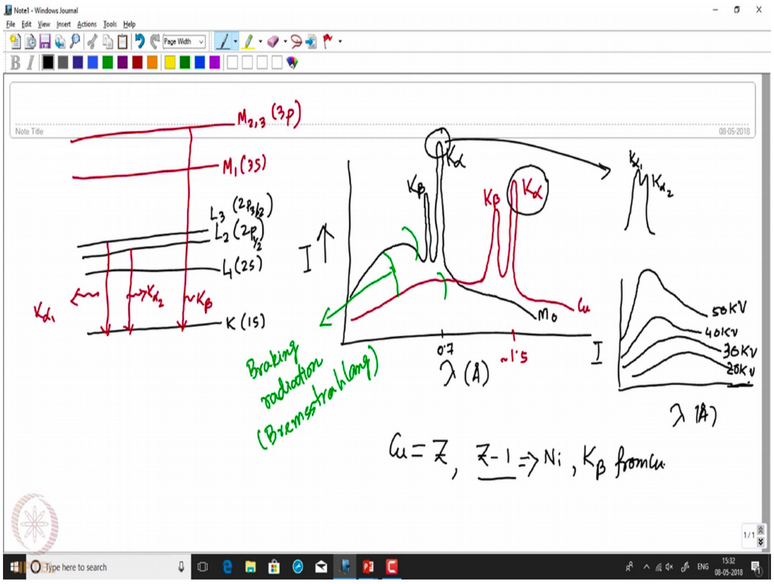

$Cu = Z$, $\underline{Z-1} \Rightarrow Ni$, K_β from Cu

So, for that nature has also given us the tool. Suppose, if we are using copper as a source, if we are using the copper tube, we need to use this copper K alpha radiation, and we should eliminate the corresponding K beta radiation. So, how can one do that this copper has the atomic number Z, and if we use the element which has element atomic number Z minus 1 that particular element turns out to be nickel. This nickel can be used as a filter, which will eliminate the radiation of K beta from copper.

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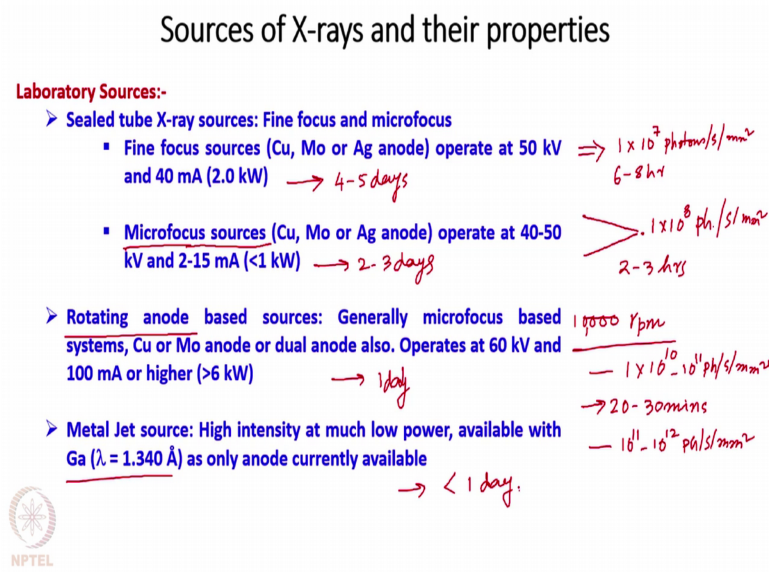

Sources of X-rays and their properties

Laboratory Sources:-

- Sealed tube X-ray sources: Fine focus and microfocus
  - Fine focus sources (Cu, Mo or Ag anode) operate at 50 kV and 40 mA (2.0 kW) → 4-5 days ⇒ 1×10^7 photons/s/mm^2 6-8 hr
  - Microfocus sources (Cu, Mo or Ag anode) operate at 40-50 kV and 2-15 mA (<1 kW) → 2-3 days > 1×10^8 ph./s/mm^2 2-3 hrs
- Rotating anode based sources: Generally microfocus based systems, Cu or Mo anode or dual anode also. Operates at 60 kV and 100 mA or higher (>6 kW) → 1 day 10,000 rpm — 1×10^{10} - 10^{11} ph/s/mm^2 → 20-30 mins
- Metal Jet source: High intensity at much low power, available with Ga (λ = 1.340 Å) as only anode currently available — 10^{11} - 10^{12} ph/s/mm^2 → < 1 day.

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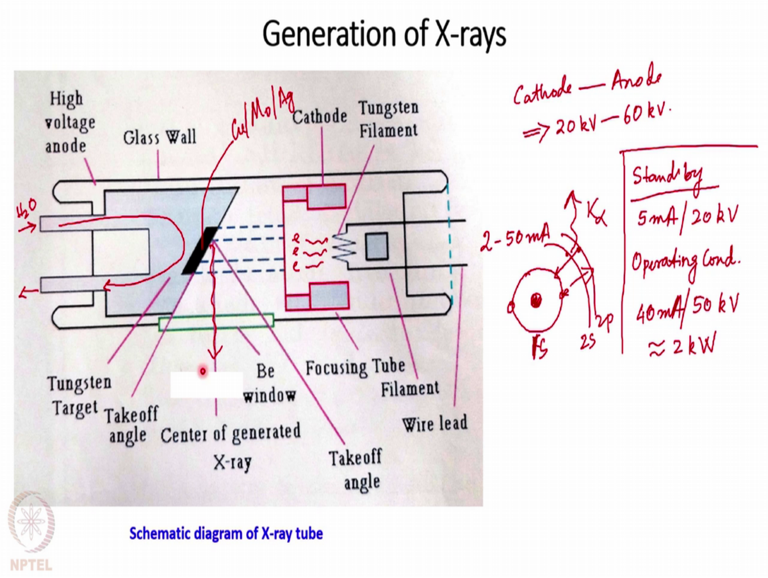
Generation of X-rays



Schematic diagram of X-ray tube

So, as a result if we use a nickel filter in the in front of this X-ray beam so, what comes out will be filtered and as a result we will get only copper K alpha radiation. So, similarly for molybdenum also we can use the filter that is having Z equal to 1 1 minus Z minus 1 that is niobium as a filter.

So, in the laboratory sources, we have a variety of X-ray sources. We can use sealed tube X-ray sources. And in that also we have two options; a fine focus, and the micro focus source. A fine focus source with copper, molybdenum or silver anode, generally operates at around 40 kilo volt and 40 milliamps, and it gives you about 2 kilowatt of energy. And that is the most common source of radiation that we use in many X-ray diffractometer laboratories. The modern X-ray diffractometers come with micro focus sources, where the X-ray beam. The beam that we comes out of the tube is focused on the X-ray on the crystal. As a result of this focusing, the intensity of the beam on the crystal increases.

So, if we assume the intensity of X-rays of that part kind of power on the crystal is giving you about 1 into 10 to the power 7 photons per second per millimeter square, the same flux that we will get on the crystal using micro focus source will increase to about 1 into 10 to the power 8 photons per second per millimeter square. So, that means we will get about 10 times increase in the intensity of that beam on the crystal. As a result, what will happen is it will reduce our data collection time. So, with the advantage of micro focus sources, we can collect data at much much faster time, instead of spending several hours using a standard X-ray tube.

The next intensity source is a rotating anodes based source, where the anode that we have talked about in the previous class, which was actually fixed. Here the anode rotates at very high speed at about 10,000 rpm. And then we can use a much much higher flux of electrons falling on the anode, which then generates X- rays in the range falling at about 1 into 10 to the power 10, sometimes even 10 to the power 11 photons per second per square millimeter.

So, now this microfocused the based rotating, and microfocus rotating anode based sources can lead to enormous high energy on the crystal, and reducing the data collection time to about 20 to 30 minutes. Whereas, in case of a sealed tube source, the data collection time was about 6 to 8 hours, with microfocus source it can come down to 2 to 3 hours. And now, with rotating anode this can be done in 20 to 30 minutes.

The further advancement of this source has come up with a metal jet source, where liquid gallium is used as a source. And with this we could achieve the intensity very similar to this 10 to the power 11 to 10 to the power 12 photons per second per square millimeter. And it gives you a very high intensity on the source. On the crystal as a result, the data collection trying further reduces. As a result, we can collect large number of crystal data in one day; and as I indicated in the previous lecture, for determination of electron densities in between the two molecules. In crystalline state, we need to collect data up to a very high angle of two theta.

So, in that case we need to collect a large amount of data, and that kind of data using a standard fine focus source may take about 4 to 5 days. A micro focus source can do it in about 2 to 3 days. Rotating anode can do it in about a day. And this may be able to do it less than 1 day, so that kind of advancement can be achieved with a very very high intensity source.

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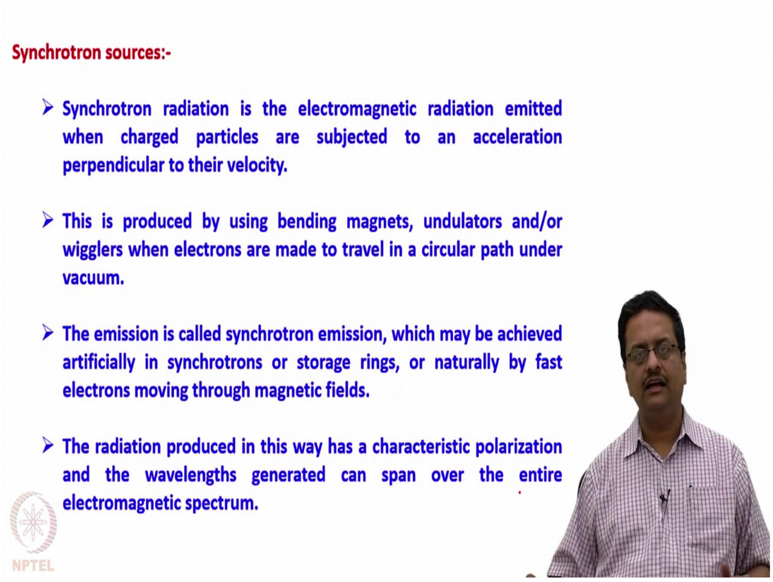

Synchrotron sources:-

- Synchrotron radiation is the electromagnetic radiation emitted when charged particles are subjected to an acceleration perpendicular to their velocity.
- This is produced by using bending magnets, undulators and/or wigglers when electrons are made to travel in a circular path under vacuum.
- The emission is called synchrotron emission, which may be achieved artificially in synchrotrons or storage rings, or naturally by fast electrons moving through magnetic fields.
- The radiation produced in this way has a characteristic polarization and the wavelengths generated can span over the entire electromagnetic spectrum.

The next higher intensity source that we can think of is synchrotron radiation, which is not available in most of the countries that are very few number of synchrotron facilities around the world. But, as you may be aware that synchrotron radiation is the electromagnetic radiation emitted, when charged particles are subjected to an acceleration perpendicular to their velocity. And this is produced using bending magnets, undulators and wigglers when the electrons are made to travel in a circular path under vacuum at very very high velocity.

So, the emission that we get while bending these electrons from their path is called the synchrotron radiation, which may be achieved artificially in synchrotron or storage rings or naturally by fast electrons moving through magnetic fields. The radiation produced in this way has characteristic polarization, and the wavelength generated can be can span over the entire range of electromagnetic spectrum, depending on the strength of the magnets or undulators or wigglers that are used to bend the highly well highly accelerated electrons.

So, one can do experiments in uv region; one can do in visible region; one can do experiments in IR and so on. And for X-rays we use these wave intensity this synchrotrons facilities in the range of about 0.2 to 0.3 angstrom to 1.8 to 2 angstrom wavelength region.

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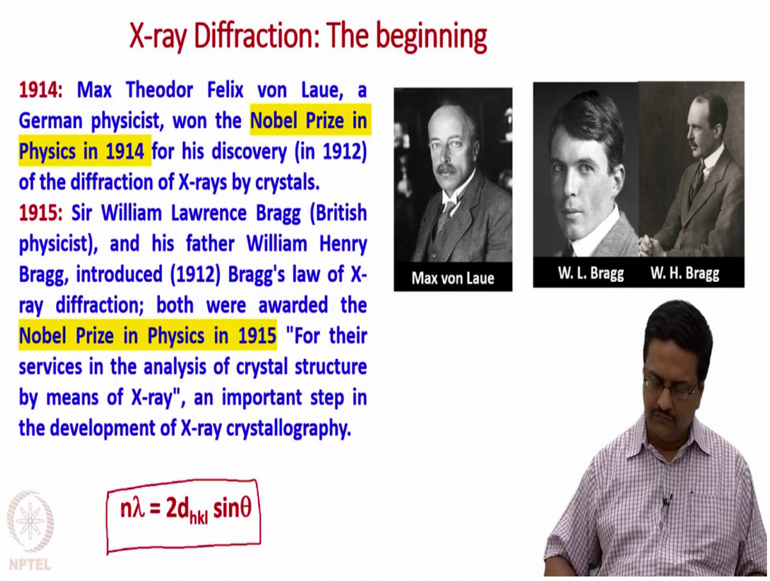

X-ray Diffraction: The beginning

1914: Max Theodor Felix von Laue, a German physicist, won the Nobel Prize in Physics in 1914 for his discovery (in 1912) of the diffraction of X-rays by crystals.

1915: Sir William Lawrence Bragg (British physicist), and his father William Henry Bragg, introduced (1912) Bragg's law of X-ray diffraction; both were awarded the Nobel Prize in Physics in 1915 "For their services in the analysis of crystal structure by means of X-ray", an important step in the development of X-ray crystallography.

$$\boxed{n\lambda = 2d_{hkl} \sin\theta}$$

So, now let us know little bit about the beginning of X-ray diffraction, which is now about hundred four-five years old in 1914 Max von Laue first received his Nobel Prize in Physics for the discovery of the phenomena that X-rays are being diffracted by a crystalline material. He was the first person to show that the X-rays can be used to characterize crystalline materials. Following his discovery and explanation, two people William Lawrence Bragg a British physicist and his father William Henry Bragg, they introduced Braggs law of X-ray diffraction, and both were simultaneously awarded Nobel Prize in Physics in 1915 for their services, in the analysis of crystal structure by means of X-ray an important step in the development of X-ray crystallography.

So, you can see the photographs of Max von Laue, and William Bragg and Henry Lawrence Bragg sorry, William Lawrence Bragg and William Henry Bragg. And, here is the very simple formula that they proposed by seeing that X-ray diffraction pattern from crystalline materials are characteristic of the compound that are being analyzed.

So, in this particular simple expression, which we will derive in a later class, it shows that it has relationship with a theta that is the angle of diffraction. This d h k l indicates the, inter planar spacing in the material, that we are talking about, and the lambda that is the wavelength of experiment. So, if we use copper, the lambda value is 1.54; if we use molybdenum it is 0.71 and so on. And this n is an integer, in general we take it as 1, because, we only are talked about first order reflection; but the same can be second order; third order or nth order reflection, so that is the order of reflection n.

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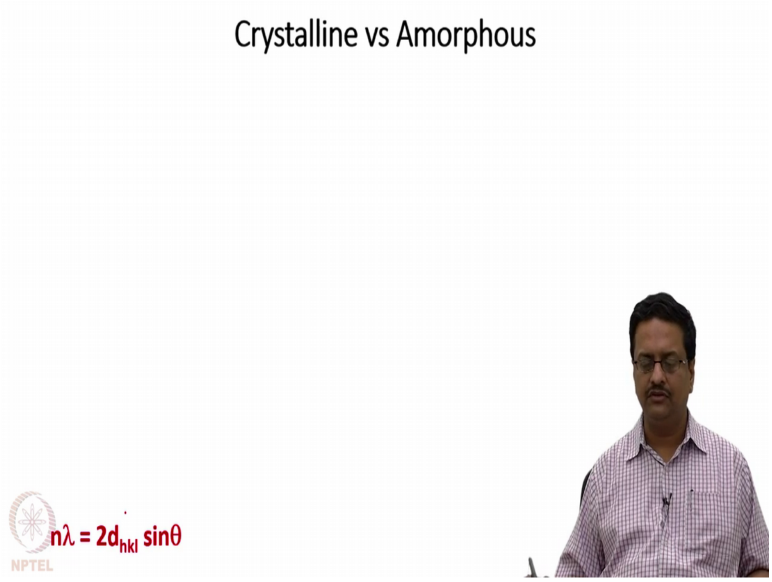

Crystalline vs Amorphous

$n\lambda = 2d_{hkl} \sin\theta$

So, now how do we know what sample is crystalline or a sample is amorphous by doing any X-ray diffraction analysis.

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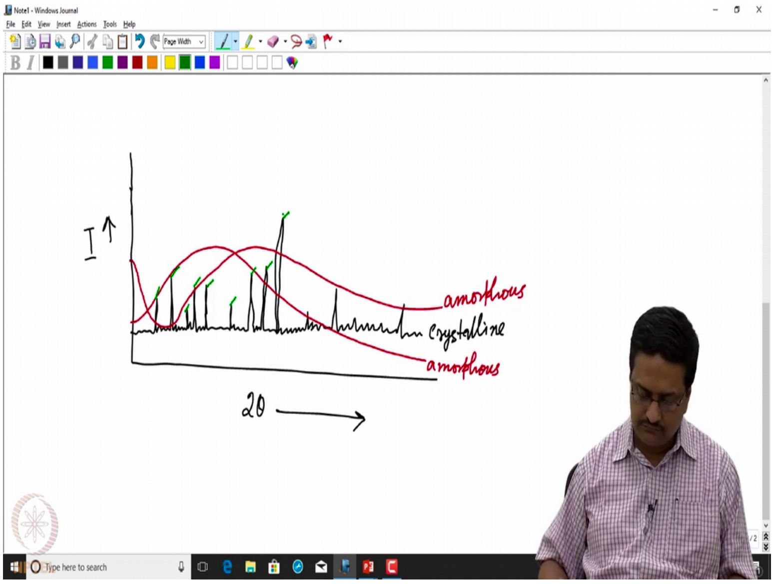

When we shine X-rays on a crystalline substance, we can record its powdered X-ray diffraction pattern. And the pattern would look like the way I am drawing. We plot intensity in the y-axis, and the 2 theta that angle or diffraction in the x-axis. And for a crystalline substance, this would result into a pattern like these with some peaks, some gap, and some tall peaks and so on.

So, this wavy peaky background signal is coming from a crystalline substance. If this particular compound was amorphous, we would have either seen something like this or maybe something like that or anything of this sort, where you do not see any peak, but what you see is just a hump. So, this particular the phenomena distinguishes the crystalline substance, from a non-crystalline substance, amorphous substance.

Now, the important aspect is that what is the significance of those peaks, you are seeing that the crystalline material has peaks. And wherever there is nothing there is a very flat background. So, these peaks signify the internal or spacing's that are responsible for X-ray diffraction following Braggs law. So, in a future class, we will discuss about these peaks how to identify those peaks how to what gives rise to those peaks during the X-ray diffraction.

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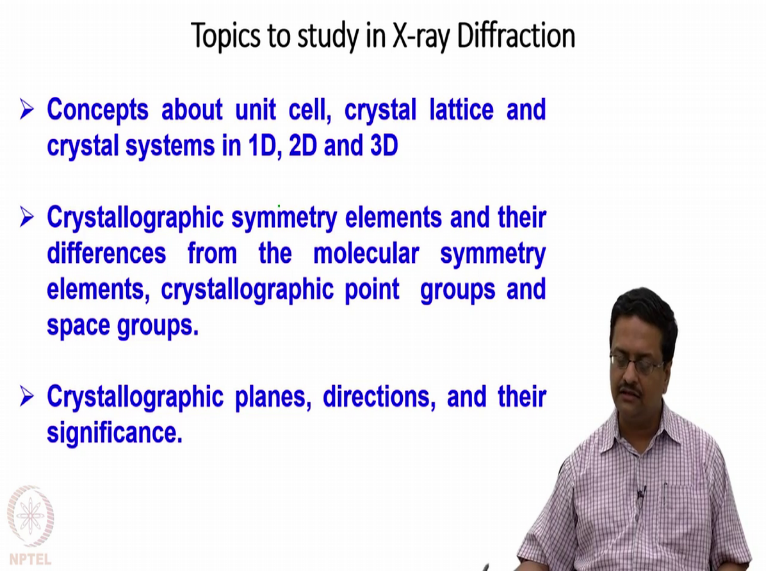

Topics to study in X-ray Diffraction

- Concepts about unit cell, crystal lattice and crystal systems in 1D, 2D and 3D
- Crystallographic symmetry elements and their differences from the molecular symmetry elements, crystallographic point groups and space groups.
- Crystallographic planes, directions, and their significance.

So, in the next part of today's lecture, we will start understanding the concepts about unit cells, crystal lattice and crystal systems in 1D, 2D and 3D. Crystallographic symmetry elements and their differences from the molecular symmetry elements, crystallographic point groups, and space groups. And in the following lectures, we will continue these crystallographic planes directions and their significance.

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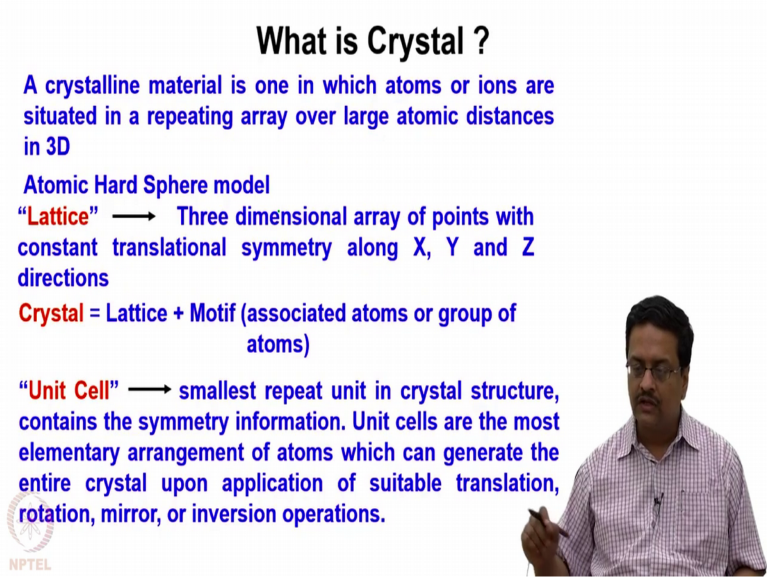

What is Crystal ?

A crystalline material is one in which atoms or ions are situated in a repeating array over large atomic distances in 3D

Atomic Hard Sphere model

"Lattice" ⟶ Three dimensional array of points with constant translational symmetry along X, Y and Z directions

Crystal = Lattice + Motif (associated atoms or group of atoms)

"Unit Cell" ⟶ smallest repeat unit in crystal structure, contains the symmetry information. Unit cells are the most elementary arrangement of atoms which can generate the entire crystal upon application of suitable translation, rotation, mirror, or inversion operations.

So, first of all what is a crystal? A crystalline material is one in which the atoms are ions are situated in a repeating array over the large atomic distances in 3D. So, suppose in this room, we have one atom in at this particular position; in the next room on my right, it will have the same position; in the following room on the further right, we will have the same atom. So, this is periodic in one direction. And the same periodicity is valid in both X, Y and Z direction, so that periodicity is the most important aspect in crystal structure, and that has to be always maintained to have a crystal lattice.

So, what is a lattice? A lattice is a three dimensional array of points in space at constant translational symmetry, along X, Y and Z. What is a crystal? A crystal is a combination of lattice, with a motif which is the association of atoms, groups of atoms or ions. So, a crystal is formed with a particular lattice having a particular three-dimensional separation, and then the three-dimensional array has a set of molecules or ions placed at equal distance in three-dimension.

What is unit cell? Unit cell is the smallest repeat unit in the crystal structure that is repeated in three-dimension X, Y and Z. And inside the unit cells have the elements, molecules, ions present in that; and those molecules ions follow a particular symmetry inside the unit cell, and that symmetry is then maintained in three-dimension in all the unit cells, adjacent to it, so that is how the crystal lattice is drawn.

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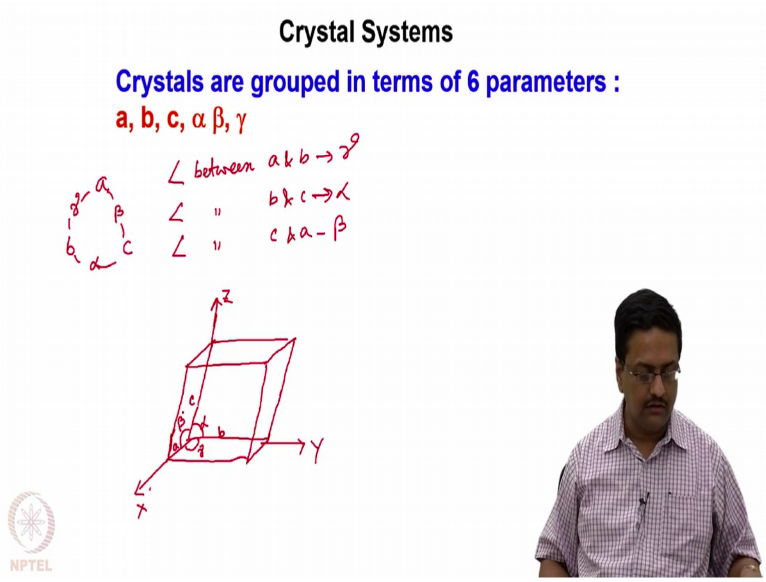

Crystal Systems

Crystals are grouped in terms of 6 parameters :

a, b, c, α β, γ

∠ between a & b → γ
∠ " b & c → α
∠ " c & a – β

So, when we try to understand that what are the different types of lattices possible. We need to know about the crystal systems. Crystal systems are understood by 6 parameters namely a, b, c, alpha, beta and gamma; a, b, c are the edge lengths; and alpha, beta, gamma are the angles between the edge lengths. So, now to remember this easily, if I write a, b, c in a triangular manner, and write alpha opposite to a; beta opposite to b; and gamma opposite to c; and then from this circle, then it means the angle between a and b is gamma; angle between b and c is alpha; and the angle between c and a is beta.

So, now if I try to draw a very general lattice, which is a total non- symmetric lattice, where a, b, c are not same; alpha, beta, gamma are not same. And this particular direction is X; this direction is called the Y; and this direction is called the Z direction. So, here the distance along X is called a; the distance along Y is called b; and the distance along Z is called c. So, the angle between a and b is gamma; angle between b and c is alpha; and the angle between c and a is called the beta, is it clear. So, in this case, we need to remember this strategy, how we identify this a, b and c along with the corresponding directions.

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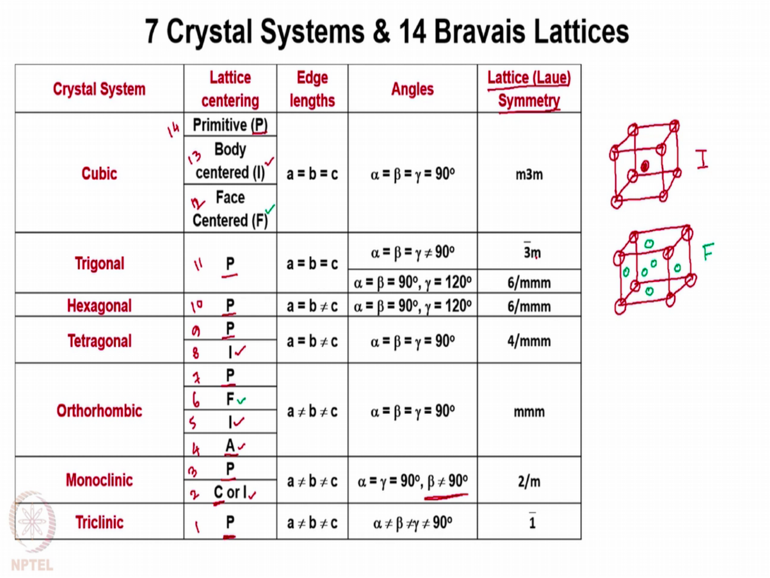

7 Crystal Systems & 14 Bravais Lattices

Crystal System	Lattice centering	Edge lengths	Angles	Lattice (Laue) Symmetry
Cubic	14 Primitive (P)	a = b = c	α = β = γ = 90°	m3m
	13 Body centered (I) ✓			
	12 Face Centered (F) ✓			
Trigonal	11 P	a = b = c	α = β = γ ≠ 90°	$\bar{3}$m
			α = β = 90°, γ = 120°	6/mmm
Hexagonal	10 P	a = b ≠ c	α = β = 90°, γ = 120°	6/mmm
Tetragonal	9 P	a = b ≠ c	α = β = γ = 90°	4/mmm
	8 I ✓			
Orthorhombic	7 P	a ≠ b ≠ c	α = β = γ = 90°	mmm
	6 F ✓			
	5 I ✓			
	4 A ✓			
Monoclinic	3 P	a ≠ b ≠ c	α = γ = 90°, β ≠ 90°	2/m
	2 C or I ✓			
Triclinic	1 P	a ≠ b ≠ c	α ≠ β ≠ γ ≠ 90°	$\bar{1}$

So, now based on these 6 parameters, which we talked about the lattice parameters a, b, c, and the angles alpha, beta, and gamma, we can identify crystal systems in several different groups. The most symmetric one that we are familiar with is a cubic system, where the edge lengths are a, b and c all are same, a equal to b equal to c; and the angles alpha, beta, gamma are all equal at 90 degree, so this is called the crisp cubic system. The next symmetric it is the trigonal, where a equal to b equal to c; alpha equal to beta equal to gamma, but not equal to 90 degree. How do we get a trigonal system, if we take a cube, and then distort it along the diagonal, the edge lengths will not change, but the three angles will change simultaneously in the same manner there is a leak into a trigonal system.

This trigonal system can be a arranged in two different ways, we can consider as alpha beta equal to 90 degree; and gamma 120 degree; but it is one type of lattice. The second the next symmetric is hexagonal, where a equal to b not equal to c; alpha and beta are 90 degree; and gamma is 120 degree. The next one is tetragonal, where a equal to b not equal to c; but alpha, beta, gamma are all 90 degree.

The next one in symmetry line comes as orthorhombic. Now, you see that the similarity of a, b, c is broken, a not equal to b not equal to c; alpha, beta and gamma all are equal are 90 degree. The second from the bottom is monoclinic, where a, b, c are not same; alpha and gamma are 90 degree; and beta is not 90 degree. And the most unsymmetrical is triclinic, where this a, b, c, s are not same; alpha, beta, gamma are also not 90 degree. So, these most un-symmetric to most symmetric crystal systems are identified here. Now, these crystal systems which we are talking about the lattices can have centerings.

So, when we have a cube which has 8 corners, so in case of that if you have atoms or molecules associated with the corners only that lattice is called the primitive lattice. So, this primitive lattice is the most common lattice that is observed, and as you see here in the second column, where we have identified lattice centering every system has a primitive type of lattice, which is here primitive, monoclinic as a primitive, orthorhombic has hexagonal sorry tetragonal, hexagonal, trigonal and primitive in case of cube.

Now, then if we have the center of the cube also having one particular atom or group of atoms as same as that of the cube corner atoms, we call it as the body centered lattice or I lattice, so that body centered lattice is present in monoclinic, orthorhombic, tetragonal and cubic. The next type of lattice that one can think of is a face centered lattice, which actually means that along with the 8 corner atoms what we have our atoms had faces of every side, so those six faces have six atoms located at the center of the face. So, this becomes a face centered lattice, we write it as F. So, in this case what we see is in case of orthorhombic, we have a face centered lattice. And in case of cubic, we have a face centered lattice.

So, now what we have here, in case of monoclinic system is that the monoclinic C, and monoclinic I lattice are one and the same. And in case of orthorhombic, I have A lattice. This C lattice indicates that in case of monoclinic system only, we considered the b axis to be unique that is why, the beta angle is non 90 degree. And when we say b beta is non 90, b is the unique axis, then the plane which is perpendicular to C that is the plane a b, which the face is perpendicular to C is centered. And that C centered lattice is considered as one of the Bravais lattices. I have seen C or I, so we will see how a C centered lattice can be converted to I centered lattice in the next lecture.

And here in case of orthorhombic, we have A centered lattice. See in case of orthorhombic, you have three sides a, b, and c, and they are not same. So, conventionally if only one parallel face of orthorhombic lattice is centered that lattice is termed as A lattice, and that particular face is designated to be the A face that means, it is the b c plane in which these atom is centered.

So, now if we try to count, how many different lattices are possible in case of these 14 these 7 crystal systems, so we have 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14. So, these are called the 14 bravais lattices that are possible out of these 7 crystal systems. Now, on the extreme right hand side column, I have highlighted the lattice symmetry or the Laue symmetry of these groups. And we see that the symmetries that are indicated here are 1 bar 2 by m mmm, 4 by mmm, 6 by mmm, 3 bar m and m 3 m. So, we will discuss about this when we get to know about the crystallographic point groups, and how these notations are introduced in this particular type of understanding.

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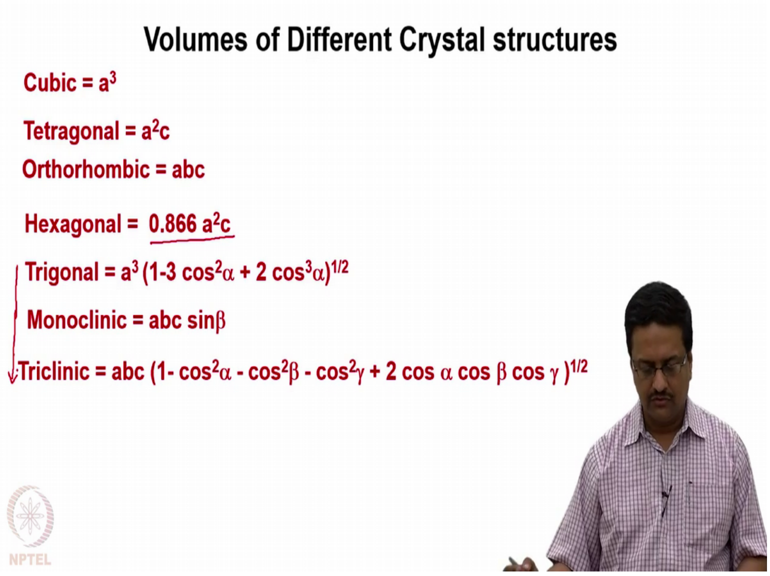

Volumes of Different Crystal structures

Cubic = a^3

Tetragonal = a^2c

Orthorhombic = abc

Hexagonal = $\underline{0.866\ a^2c}$

Trigonal = $a^3 (1-3\cos^2\alpha + 2\cos^3\alpha)^{1/2}$

Monoclinic = $abc \sin\beta$

Triclinic = $abc\,(1-\cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma)^{1/2}$

So, when one knows how the lattice parameters can be varied for different systems, we need to know about how to calculate the volume of those lattices. Here are, some standard formula that we use to determine the volume of these crystal lattices. For cubic, the system is very simple; it is a cube. For tetragonal, it becomes a square c; orthorhombic is a, b, c. And then when you come to hexagonal as the angle becomes non 90 degree, we get to more complicated formula like 0.866 a square c. I would like you to look at a textbook, how to derive this because we do not have enough time to derive all these in the particular course.

And then as and when the symmetry reduces from trigonal to monoclinic to triclinic, you can see the formula becomes really complicated to determine the unit cell volume. But, these are all required to determine the volume of these crystal structures. So, in this part of the lecture, we have discussed about the generation of X-rays, we have talked about how the lattices are there bravais lattices and the volumes of unit cells. In the following lecture, we will talk about crystallographic symmetry.