Characterization of Construction Materials
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Lecture 14
X Ray Diffraction Crystal Systems and History of XRD Part 1

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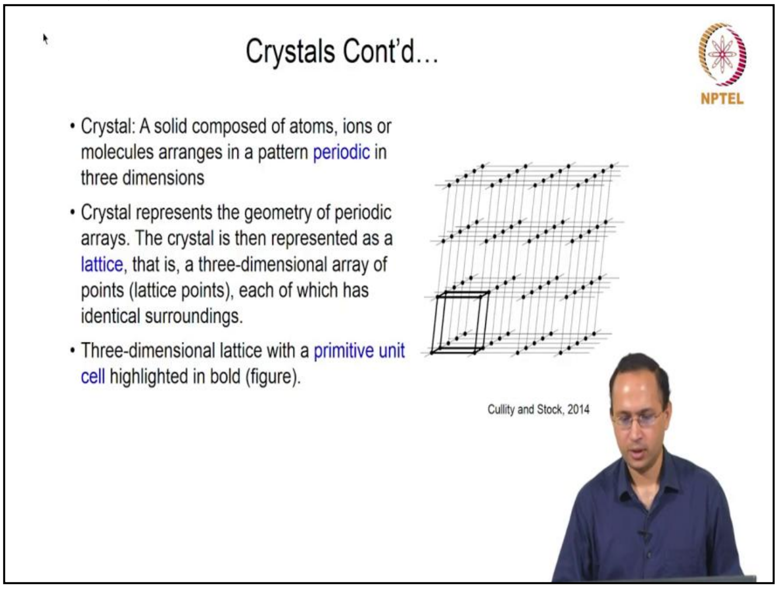

Crystals Cont'd…

- Crystal: A solid composed of atoms, ions or molecules arranges in a pattern periodic in three dimensions
- Crystal represents the geometry of periodic arrays. The crystal is then represented as a lattice, that is, a three-dimensional array of points (lattice points), each of which has identical surroundings.
- Three-dimensional lattice with a primitive unit cell highlighted in bold (figure).

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Hi everyone, we will continue our lecture on X-ray diffraction. So, before we proceed we'll review what we studied in the last lecture. So, in the last lecture we saw what are X-rays? How X-rays are produced and discussed about the characteristic spectrum. This gives rise to the monochromatic nature of X-rays. Then we also discussed about the crystal systems. And we ended our discussion on that, but before we proceed, I will just again review basics of crystal systems.

So we are talking about the periodic arrangement of lattice. You have a long-range order in crystals. So, first thing we looked at was the unit cell. So, you have this unit cell and it is arranged in three dimensions, so it is a crystal. So, first we looked at only unit cell. So, we defined unit cell by 6 different parameters, length along a,b,c axes and interaxial angles, α, β, γ. So, there are different classes.

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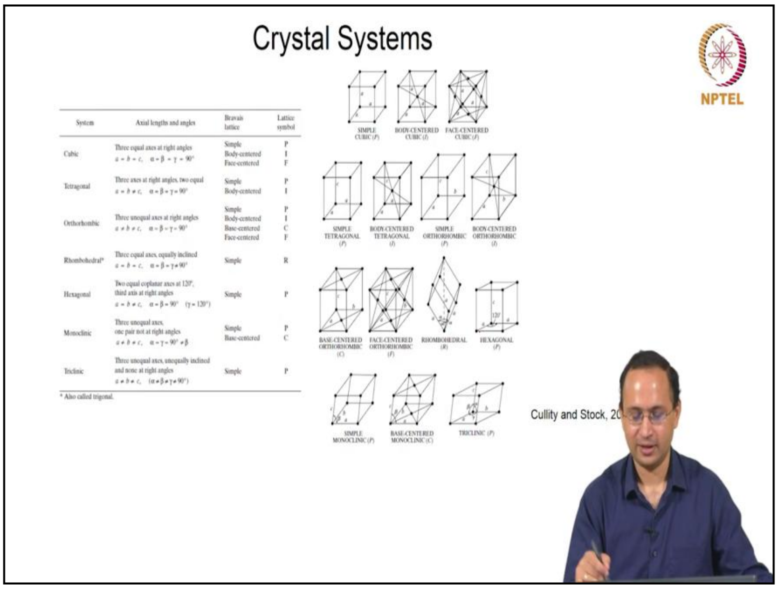

Crystal Systems

System	Axial lengths and angles	Bravais lattice	Lattice symbol
Cubic	Three equal axes at right angles $a = b = c,\quad \alpha = \beta = \gamma = 90°$	Simple Body-centered Face-centered	P I F
Tetragonal	Three axes at right angles, two equal $a = b \neq c,\quad \alpha = \beta = \gamma = 90°$	Simple Body-centered	P I
Orthorhombic	Three unequal axes at right angles $a \neq b \neq c,\quad \alpha = \beta = \gamma = 90°$	Simple Body-centered Base-centered Face-centered	P I C F
Rhombohedral*	Three equal axes, equally inclined $a = b = c,\quad \alpha = \beta = \gamma \neq 90°$	Simple	R
Hexagonal	Two equal coplanar axes at 120°, third axis at right angles $a = b \neq c,\quad \alpha = \beta = 90° \quad (\gamma = 120°)$	Simple	P
Monoclinic	Three unequal axes, one pair not at right angles $a \neq b \neq c,\quad \alpha = \gamma = 90° \neq \beta$	Simple Base-centered	P C
Triclinic	Three unequal axes, unequally inclined and none at right angles $a \neq b \neq c,\quad (\alpha \neq \beta \neq \gamma \neq 90°)$	Simple	P

* Also called trigonal.

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We discussed here these are 7 different classes, 7 different crystal systems.

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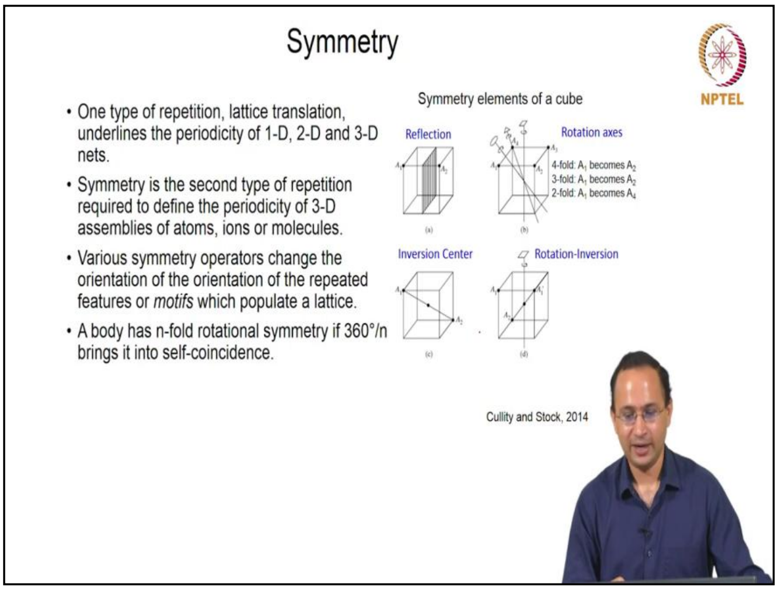

Symmetry

- One type of repetition, lattice translation, underlines the periodicity of 1-D, 2-D and 3-D nets.
- Symmetry is the second type of repetition required to define the periodicity of 3-D assemblies of atoms, ions or molecules.
- Various symmetry operators change the orientation of the orientation of the repeated features or *motifs* which populate a lattice.
- A body has n-fold rotational symmetry if 360°/n brings it into self-coincidence.

Symmetry elements of a cube

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And we discussed about the symmetry. So, you can have reflection, you can have rotation axis, you can see how we have a 4-fold symmetry in cube 3-fold symmetry, 2-fold symmetry and then you have inversion center, rotation-inversion symmetry.

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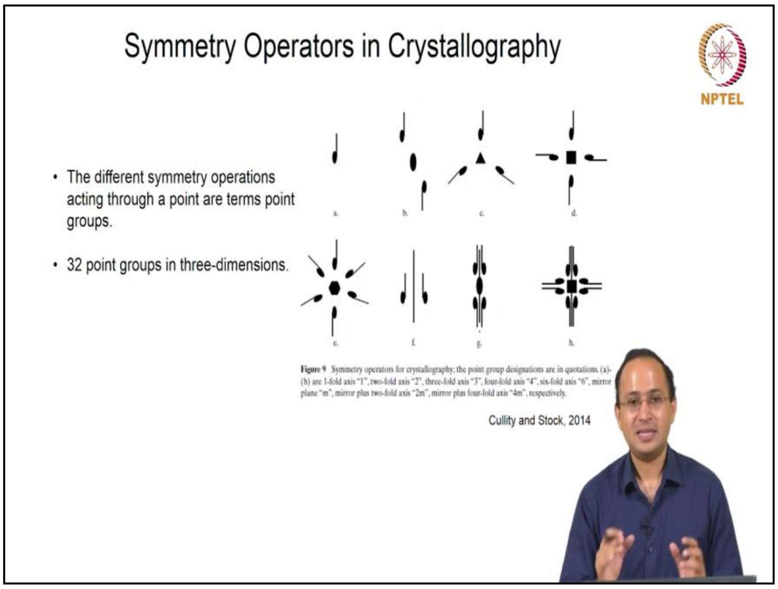

Symmetry Operators in Crystallography

- The different symmetry operations acting through a point are terms point groups.
- 32 point groups in three-dimensions.

Figure 9 Symmetry operators for crystallography; the point group designations are in quotations. (a)-(h) are 1-fold axis "1", two-fold axis "2", three-fold axis "3", four-fold axis "4", six-fold axis "6", mirror plane "m", mirror plus two-fold axis "2m", mirror plus four-fold axis "4m", respectively.

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So, basically these symmetry operations are used in crystallography and the different symmetry operations acting through a point are termed as point groups. So, there are 32 point groups, basically 32 symmetry operations, in 3 dimensions. So, now you know about the unit cell.

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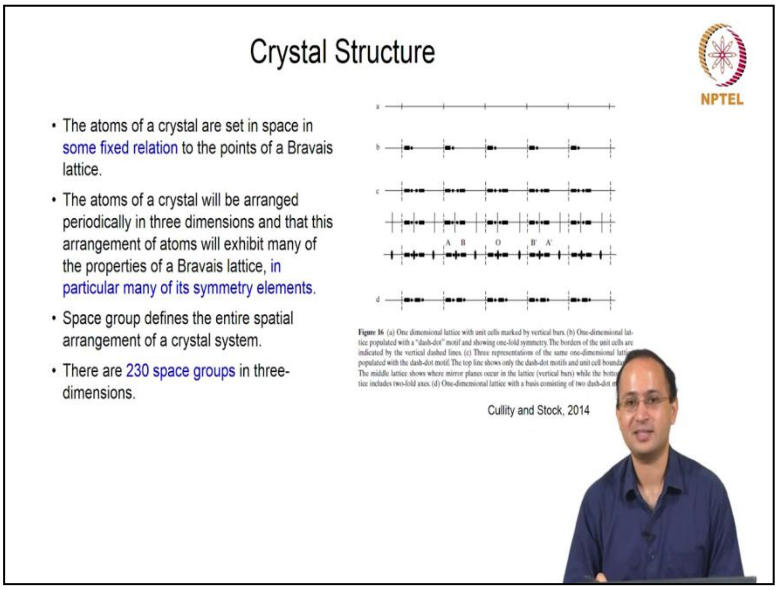

Crystal Structure

- The atoms of a crystal are set in space in some fixed relation to the points of a Bravais lattice.
- The atoms of a crystal will be arranged periodically in three dimensions and that this arrangement of atoms will exhibit many of the properties of a Bravais lattice, in particular many of its symmetry elements.
- Space group defines the entire spatial arrangement of a crystal system.
- There are 230 space groups in three-dimensions.

Figure 16 (a) One dimensional lattice with unit cells marked by vertical bars. (b) One-dimensional lattice populated with a "dash-dot" motif and showing one-fold symmetry. The borders of the unit cells are indicated by the vertical dashed lines. (c) Three representations of the same one-dimensional latti populated with the dash-dot motif. The top line shows only the dash-dot motifs and unit cell bounda The middle lattice shows where mirror planes occur in the lattice (vertical bars) while the botto tice includes two-fold axes. (d) One-dimensional lattice with a basis consisting of two dash-dot m

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Now you have to apply these symmetry operations, which will give you a crystal. Now we are talking about the real crystal structures, those are the geometric manifestations. So, the atoms of crystals are set in space in some fixed relation to the points of a Bravais lattice. We know there are 14 Bravais lattices. Now the atoms of a crystal are set in space in some fixed relation. Some fixed relation is, it could have symmetry.

And the atoms of a crystal will be arranged periodically in 3 dimensions and this arrangement of atoms will exhibit many of the properties of a Bravais lattice, in particular many of its symmetry elements. So, space group defines the entire spatial arrangement of a crystal system. Now you have a unit cell, it is getting repeated, so this whole, the space group defines the entire spatial arrangement of a crystal system.

Basically what you see here in the figure (see Slide) in ‘a’, you have this one dimensional lattice, with unit cells marked by a vertical bar, so you have one unit cell; it is a straight one-dimensional lattice. That is one example. Now you can add some features. So, in ‘b’ what do you see? This is again a one dimensional lattice. But you have this ‘dash-dot’, which you can think of as the repeating features. These are the features which are getting repeated.

Also we call these as ‘motifs’. But simply you can think of it as a repeating feature. So, here you have a dash-dot getting repeated. So, this is one dimensional lattice and this is a feature which is getting repeated, showing 1-fold symmetry. 1-fold symmetry means if you rotate this by 360°, it will come to self-coincidence. You can try it, until you rotate it to 360°, you would not get the same feature clear.

Now let us look at c. The repeating feature is ‘dash-dot, dot-dash’. That is one cell. These dashed lines (in figure) are one unit cell. So, this feature is getting repeated. This is again one dimension we are talking about. So, now you notice we have 3 representations. So, as we discussed, you see the unit cell and you see these repeating features ‘dash-dot, dot-dash’.

So think of these (solid lines marked in-between each ‘dash-dot, dot-dash) as mirror planes, so think of it as a reflection. So, that is one kind of symmetry. We have the same pattern. Now in the last one in the bottom (in ‘c’), what we see is a 2-fold axis, which means if you rotate by 180°, so you have this dash-dot, dot-dash and these are the symbols (marked in figure) for 2-fold symmetry.

So, you can try, if you rotate it by 180°, you will get the same. So, in this you now see that 2-fold axis symmetry is there, in the middle one (in ‘c’), you see just mirror planes, the same arrangement.

And now, in‘d’, what we see is a one-dimensional lattice again with a basis consisting of 2 dash-dot motifs. Basis is also motifs, basis is basically the repeating features, you have ‘dash-dot, dash-dot’.

This is the feature which is getting repeated. See, in crystal what you have is periodicity. So, now you will appreciate it. We know about the 7 crystal systems, 14 Bravais lattices, but it is also important to consider the symmetry and the way they are arranged. In real crystals when you apply those 32 points groups that we have, i.e., the symmetry operations on these Bravais lattices, then you will get a lot of space groups.

So, in reality you have only 230 unique space groups only and not more than that. That is because of these symmetry operations applied on these Bravais lattices in 3 dimensions. Simple case is when this unit cell is getting repeated and that is easy to visualize. But now, from this you can see how symmetry plays a role.

So, we will not go in detail, because crystallography in itself is a vast area but just wanted to touch upon the important principles like, what is a unit cell? What is symmetry? What are the different crystal systems we have? So we can then use that to understand the material.

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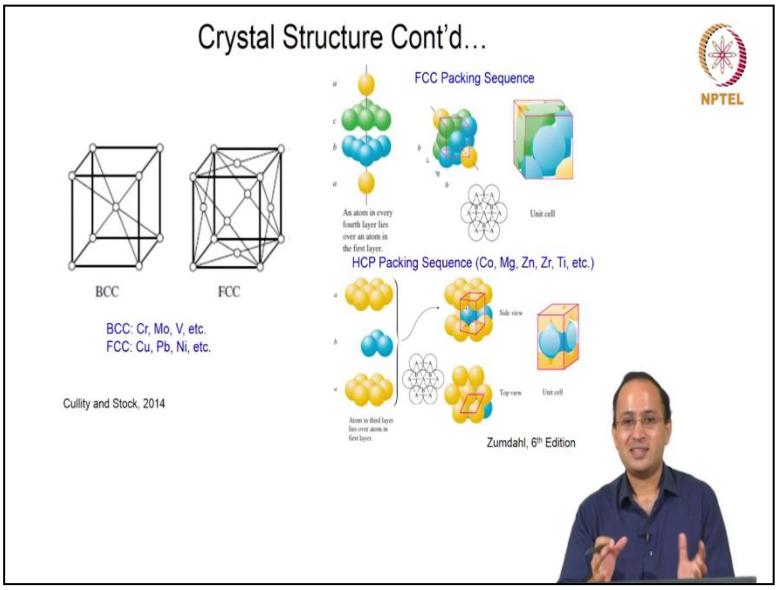

Crystal Structure Cont'd…

BCC: Cr, Mo, V, etc.
FCC: Cu, Pb, Ni, etc.

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FCC Packing Sequence

HCP Packing Sequence (Co, Mg, Zn, Zr, Ti, etc.)

Zumdahl, 6th Edition

So, we are talking about real crystal structure. One we learned about is BCC, body-centered cubic. Simple way of arranging atoms would be just to put the atoms in the corners (in BCC). So, this is BCC and it is exhibited by many metals (Cr, Mo, V, etc.) which exhibit this kind of structure. Obviously in real life you would not have this much gap here, it just shown so that it is easy to see in figure, but in real life, the spheres will be touching, because it will try to minimize that voids or maximize the density.

Another example is FCC, face-centered cubic when you put these atoms in the corners and also in the face, on each face. So, how many atoms are there in this BCC, because see in real life you have these unit cells repeating. So, each atom which is at the corner is being shared by 8. So, you can write a formula, total N will be, let us say if N_i is the inside one that is not being shared by any other unit cell.

The corner one is N_c let us see shared by 8, hence $\left(\frac{N_c}{8}\right)$, let us say N_f the face and the atom on the face will be shared by only 2, hence $\left(\frac{N_c}{2}\right)$. So, this will give you your total number of atoms. So, in BCC you have 2 atoms. Now you can calculate for FCC. So, also common packing is FCC, FCC packing sequence. So, here we see an atom in every 4th layer lies over an atom in the first layer. So, order is ABC, ABC, and ABC. Think of it like you have balls.

First layer of A, this is a simplification, you put these balls then you put B, the second layer will consist of B which will be on the voids created by A. Then similarly, you put C in the voids created by B, but then A repeats. So ABC, ABC. That is the order that gives you maximum density or maximum packing fraction. And so here you see that. This is ABC the ABC that is how it will repeat, there are only 2 ways to get the maximum density, one is this. So another way to look at it and it is nothing but, it is an FCC. If you look at this you will find out, you have to visualize, this is FCC arrangement, face-centered cubic.

Another way of packing is hexagonal closed packing, HCP. So in this, you have A,B. So, first layer consists of the A atoms, then you have second layer of B atoms, the third layer instead of C you have again A. So AB, AB, AB. That is the sequence.

It is clear from this picture. So you see A, then you have B, then you repeat A. So AB, AB, AB. That also gives you maximum packing fraction. And if you look at the side view, you will realize this is HCP, hexagonal close packing. And these are the examples. HCP is exhibited by cobalt, magnesium, zinc, zirconium, titanium. So, these are the real crystal structures. So, we would not go much in detail. Now you know what the different crystal systems are, Bravais lattices and about the symmetry. Now we will see how we can connect X-rays to crystals.

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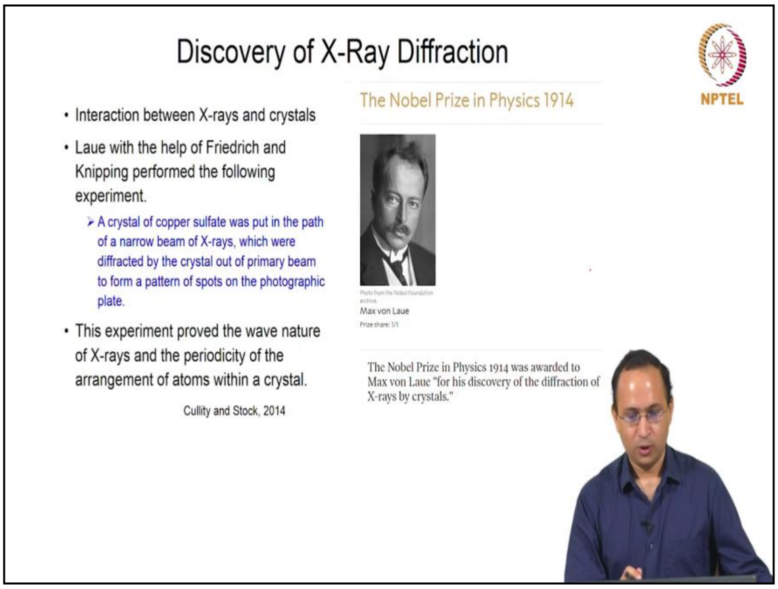

Discovery of X-Ray Diffraction

- Interaction between X-rays and crystals
- Laue with the help of Friedrich and Knipping performed the following experiment.
  - ➢ A crystal of copper sulfate was put in the path of a narrow beam of X-rays, which were diffracted by the crystal out of primary beam to form a pattern of spots on the photographic plate.
- This experiment proved the wave nature of X-rays and the periodicity of the arrangement of atoms within a crystal.

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The Nobel Prize in Physics 1914

Photo from the Nobel Foundation archive.

Max von Laue

Prize share: 1/1

The Nobel Prize in Physics 1914 was awarded to Max von Laue "for his discovery of the diffraction of X-rays by crystals."

So, again little bit of background about the discovery of X-ray diffraction. So, it is nothing but the interaction between X-rays and crystals, so Max Von Laue with the help of his experimentalist friends Friedrich and Knipping, was the first one to perform the following experiment. He put a crystal of copper sulphate in the path of a narrow beam of X-rays.

Before that, X-rays were known. X-rays were discovered in 1894. So he just put X-rays before this crystal of copper sulphate, which was diffracted by the crystals out of primary beam to form a pattern of spots on the photographic plates. He saw a very interesting pattern which had symmetry. So this experiment proved the wave nature of X-rays and the periodicity that crystals have.

We talked about the arrangement of unit cells. So, this pattern proved the wave nature of X-rays and the periodicity of the arrangement of atoms within crystals.

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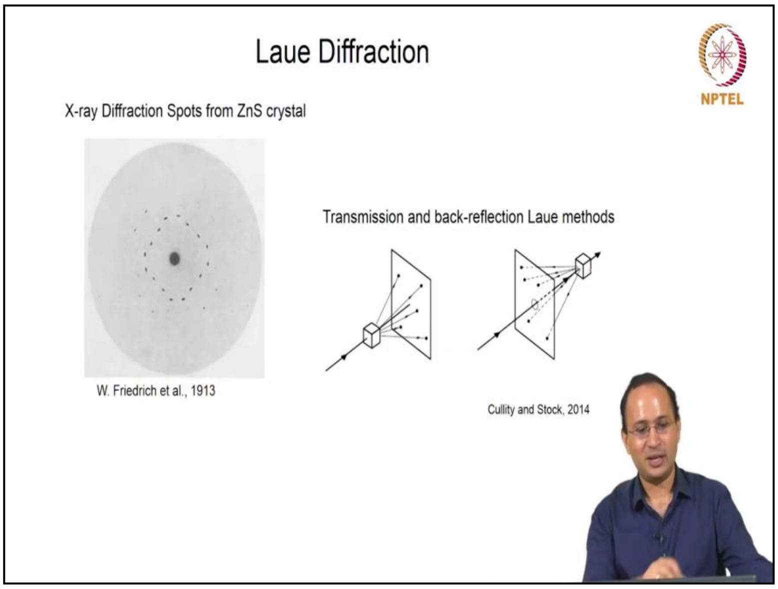

Laue Diffraction

X-ray Diffraction Spots from ZnS crystal

W. Friedrich et al., 1913

Transmission and back-reflection Laue methods

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So, this is zinc sulphide, ZnS crystal. If you put X-rays, you see these X-ray diffraction spots from the zinc sulphide crystals. So, these are called Laue spots. So, it tells you about some symmetry, some periodicity. So, for this he got a Nobel Prize in 1914 in Physics for his discovery of the diffraction of X-rays. So, this experiment tells you that X-rays can diffract crystals, because you are seeing that periodicity when you put crystals on the path of X-rays.

Here are some transmission and back-reflections Laue methods; you can see that if you put crystals here you will see these spots. Another way of looking at it is, you let the X-rays go through and then when there is a reflection you see these spots.

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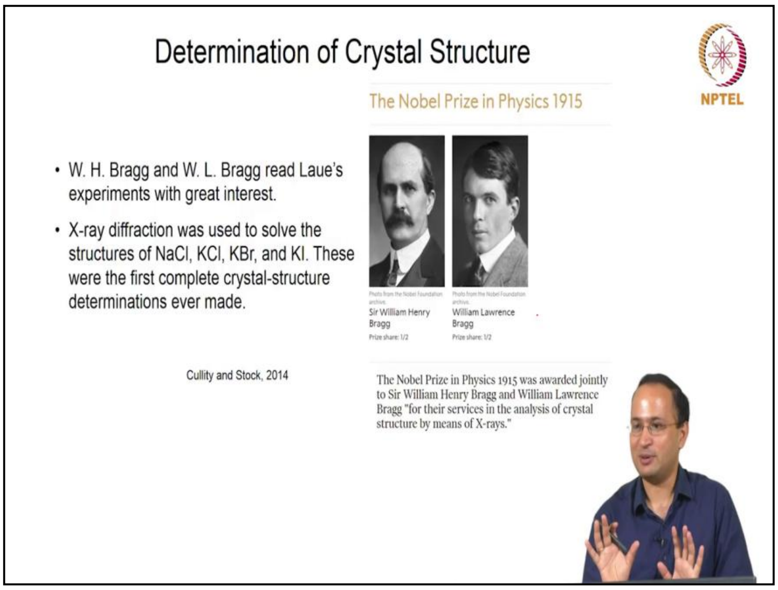

Determination of Crystal Structure

- W. H. Bragg and W. L. Bragg read Laue's experiments with great interest.
- X-ray diffraction was used to solve the structures of NaCl, KCl, KBr, and KI. These were the first complete crystal-structure determinations ever made.

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The Nobel Prize in Physics 1915

Photo from the Nobel Foundation archive.
Sir William Henry Bragg
Prize share: 1/2

Photo from the Nobel Foundation archive.
William Lawrence Bragg
Prize share: 1/2

The Nobel Prize in Physics 1915 was awarded jointly to Sir William Henry Bragg and William Lawrence Bragg "for their services in the analysis of crystal structure by means of X-rays."

Now we are not talking about the crystals, per se, we only know that X-rays when they interact with the crystal give you this pattern. Then around the same time after this came up, Bragg, they found it very interesting, they were reading these papers, Laue and with his co-authors wrote about it, that there is the interaction between X-rays and crystals. So, they were saying that is very interesting.

So, they did experiments, so father and son duo, Henry Bragg and Lawrence Bragg read Laue's experiment with great interest. X-ray diffraction was used to solve the structures of crystals of sodium chloride, potassium chloride, potassium bromide, potassium iodide. They solved the crystal structure of these compounds.

These were the first complete crystal structure determination ever made and for this, they got the Nobel Prize in 1915. In the first one, you see the interaction between X-rays and crystals, and then they with the help of X-rays solved the crystal structure. Both got the Nobel Prize for their services in the analysis of crystal structure by means of X-rays.

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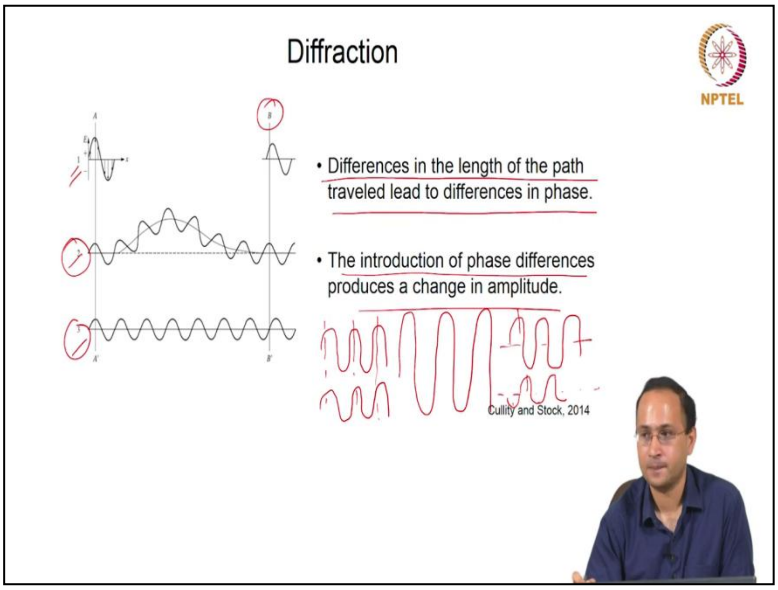

Diffraction

- Differences in the length of the path traveled lead to differences in phase.
- The introduction of phase differences produces a change in amplitude.

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So, now we will see what gives rise to diffraction. The diffraction is basically the interaction of 2 waves. So, this is a very simplistic example, suppose 1 (see in Figure) consists of 2 and 3 waves, and if you distort the 2nd wave and come to B and you look at the resultant, it will be different.

So we are talking about these interferences, when they will constructive and when they will be destructive. If they are in phase, it will be constructive interference. So, what it tells you is differences in the length of the path travelled lead to differences in the phase. So, depends on how much difference there is, and that will give you the difference in the phase. And the introduction of the phase difference produces the change in amplitude, because this phase difference then will affect the net amplitude.

Simple way of understanding this is, suppose you have 2 waves (refer drawing in slide), then we have a constructive interference. Now suppose you have this case (refer drawing in slide), so here is the peak, then you have a destructive interference because this will cancel out.

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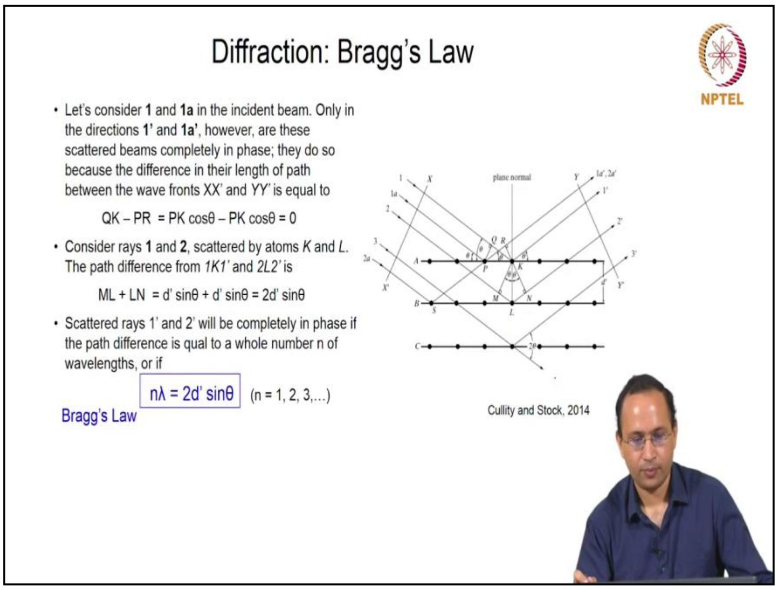

Diffraction: Bragg's Law

- Let's consider **1** and **1a** in the incident beam. Only in the directions **1'** and **1a'**, however, are these scattered beams completely in phase; they do so because the difference in their length of path between the wave fronts *XX'* and *YY'* is equal to

$$QK - PR = PK\cos\theta - PK\cos\theta = 0$$

- Consider rays **1** and **2**, scattered by atoms *K* and *L*. The path difference from *1K1'* and *2L2'* is

$$ML + LN = d'\sin\theta + d'\sin\theta = 2d'\sin\theta$$

- Scattered rays 1' and 2' will be completely in phase if the path difference is qual to a whole number n of wavelengths, or if

$$\boxed{n\lambda = 2d'\sin\theta} \quad (n = 1, 2, 3,\ldots)$$

Bragg's Law

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So, let us look at the interaction between X-rays and now we are trying to understand the crystal structure and how we can determine the crystal structure. So, you have these atoms, we are talking about crystals, so there is a periodicity, they are arranged in a systematic manner so these are the atoms in the crystals (in figure in slide). Now X-ray will interact, so you have this wave front X X', that is one wave front, incoming incident ray beam.

So, let us consider 1 and 1a in the incident beam. So you have these rays 1, 1a, 2 so what we see is, 1 will interact with K, 1a will interact with P. Let us look at 1 and 1a first. 1 and 1a interact only with the surface atoms (P and K), we are not going deep. Only in the direction 1' dash and 1a', now you see there is diffraction in this direction however, are these scattered beams completely in phase.

How do you get the difference? Basically we have (QK – PR). So, see we are looking at this incoming, this is the wave front, up to here (QP), there is no difference, and same thing beyond this (RK), there is no difference between the 2 rays. So, only difference is because of this additional QK, this ray 1 travels this much extra (QK).And 1a' travels PR, path difference and you can see from this

$$QK - PR = PK\ Cos\theta - PK\ Cos\theta = 0$$

So, these 2 rays are in phase, the path difference is 0. Earlier we saw the path difference creates the difference in phase, phase difference will lead to difference in amplitude. So far, we talked about the surface atoms but there are atoms beyond that as you go deep.

Now we will look at the second layer 'B', now consider rays 1 and 2 and distance between the 2 layers (A and B) is d'. So, what is the path difference for the rays 1 and 2? So 1 interacts with K and 2 interacts with L and 1' and 2' are the diffracted rays respectively.

again similar thing, up to here if you up to here (KM), there is no path difference between ray 1 and ray 2, i.e., both are parallel. Similarly beyond this (KN), there is no path difference. Now you have to calculate only the difference, basically this ray (2) travels this much extra (ML) and also this much (LN). So, we have to calculate (ML + LN), that is the path difference.

So what is ML? So, you know that the spacing is d'. And you have angle θ, because incident ray makes θ angle with the plane. So, using geometry, $\angle MKL = \angle LKN = \theta$, because $\angle QKP = \theta \rightarrow \angle PKM = 90 - \theta \rightarrow \angle MKL = \theta$. So, when $\angle MKL = \theta$, then $ML = d'\ Sin\,\theta$ and also $LN = d'\ Sin\,\theta$.

So, $Total\,path\,difference = 2d'\ Sin\,\theta$. So, now the scattered rays 1' and 2' will be completely in phase, if the path difference is equal to a whole number 'n' of the wavelengths. That means

$$2d'\ Sin\,\theta = n\lambda$$

Where, n = 1, 2, 3,...
Basically what we are saying is, you have a wave, and you have a λ (see Drawing in slide).
Now, if there is a path difference of λ or whole number 'n' of λ, then you will have waves in phase. Basically you are shifting the wavelength, λ, 2λ, 3λ. So, you will have a constructive interference. So, this is the Bragg condition, it is called Bragg's law, $2d'\ Sin\,\theta = n\lambda$ where n = 1, 2, 3,... that gives rise to this constructive interference or diffraction.

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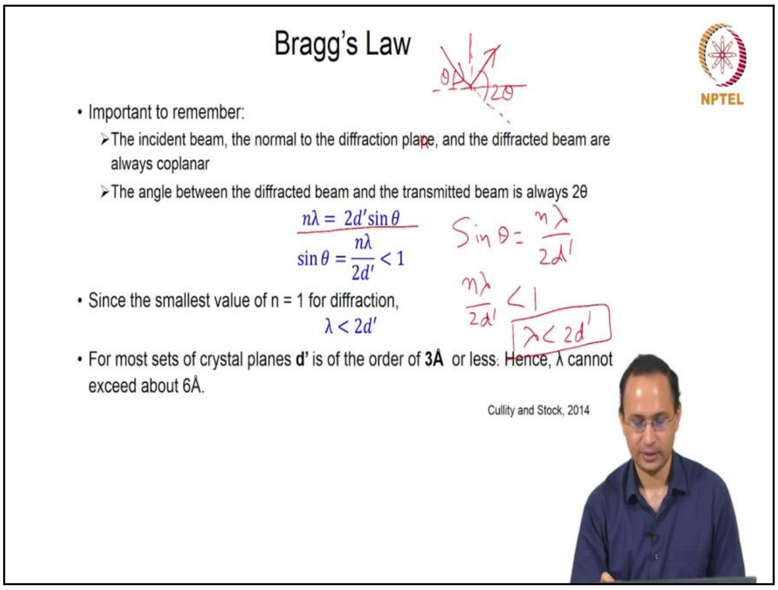

Bragg's Law

- Important to remember:
  - ➢The incident beam, the normal to the diffraction plane, and the diffracted beam are always coplanar
  - ➢The angle between the diffracted beam and the transmitted beam is always 2θ

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

$$\sin\theta = \frac{n\lambda}{2d'} < 1$$

- Since the smallest value of n = 1 for diffraction,

$$\lambda < 2d'$$

- For most sets of crystal planes **d'** is of the order of **3Å** or less. Hence, λ cannot exceed about 6Å.

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$\sin\theta = \frac{n\lambda}{2d'}$

$\frac{n\lambda}{2d'} < 1$

$\boxed{\lambda < 2d'}$

Again we will look at the Bragg's law. So it is important to remember that the incident beam, the normal to the diffraction plane, and the diffracted beam are coplanar. So, this is your incident beam, this is your diffracted beam, this is your normal to the plane diffraction plane (Refer Figure 1). All 3 are always coplanar, they will exist in the same plane.

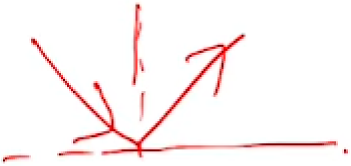

Figure 1 Incident beam, Normal to the diffraction plane, Diffracted beam

The angle between the diffracted beam and the transmitted beam is always 2θ. So, you know that angle between incident beam and diffraction plane is θ, and angle between diffracted beam and the incident beam will always be 2θ. (Refer Figure 2)

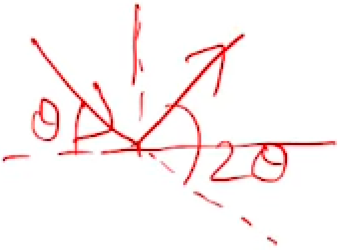

Figure 2 Angle between incident and diffracted beam

Now we know from the last slide that

$$n\lambda = 2d' \operatorname{Sin} \theta \rightarrow \operatorname{Sin} \theta = \frac{n\lambda}{2d'}$$

Now you know that Sinθ cannot be greater than 1. So you can put this limit. So it tell you that

$$\operatorname{Sin} \theta = \frac{n\lambda}{2d'} < 1$$

And since the smallest value of n is 1, so what does it give you $\lambda < 2d'$.
For most sets of crystal planes d' the spacing, is in the order of 3 Å or less.

Hence λ cannot exceed 6 Å, and that is the limit. If you are using a wavelength, because you want to know if you have a range of wavelengths and you want to pick the wavelength which can give you diffraction, it says that $\lambda < 6$Å.