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 - 03
Crystallographic Symmetries

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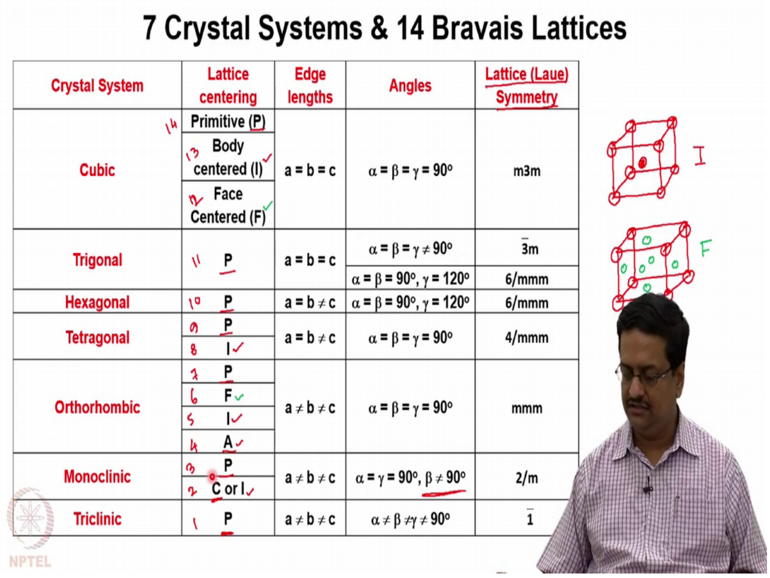

7 Crystal Systems & 14 Bravais Lattices

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

Welcome back to today's lecture on X-ray Crystallography. In the previous class, we learned about the X-ray sources, different types of X-ray sources that are known and their power how the X-rays are generated. And then we were learning about 7 crystal systems and 14 Bravais lattices. So, in that we discussed about the fact that we have in monoclinic system C and I, and I have written it as C or I, and I indicated that these two or one and the same.

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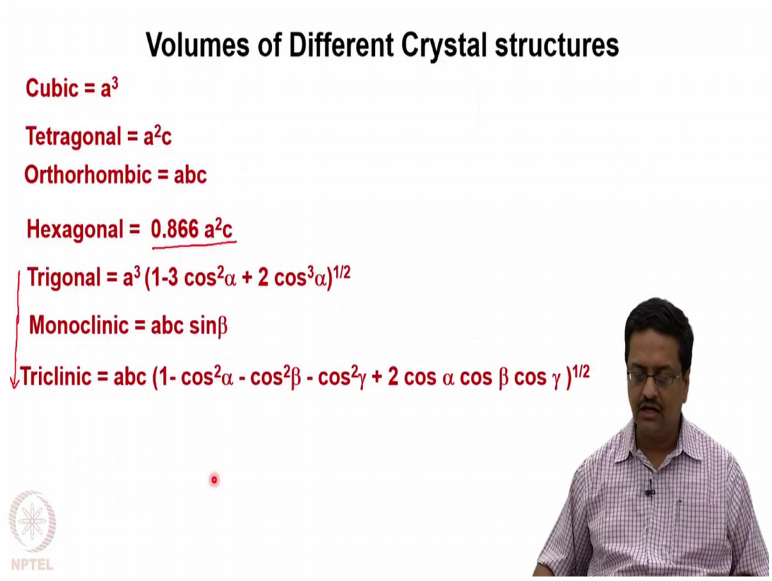

Volumes of Different Crystal structures

Cubic = a^3

Tetragonal = a^2c

Orthorhombic = abc

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

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

Monoclinic = abc $\sin\beta$

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

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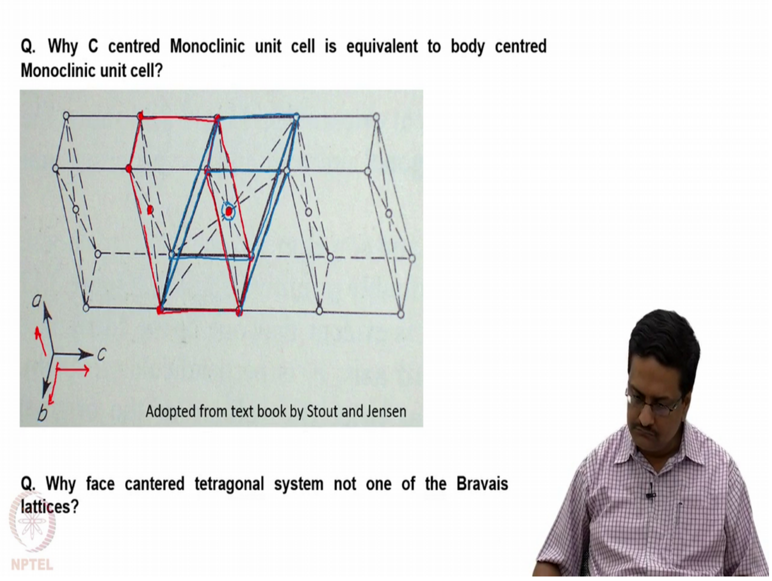

Q. Why C centred Monoclinic unit cell is equivalent to body centred Monoclinic unit cell?

Adopted from text book by Stout and Jensen

Q. Why face cantered tetragonal system not one of the Bravais lattices?

So, today we will see, how these two are same. See here in this particular figure is drawn a monoclinic unit cell with the axis as indicated here in the figure down that b axis is pointing towards us; c axis is pointing towards right, and a is the axis pointing upwards. So, in this orientation, if you consider the unit cell, connecting these points which are marking now, the unit cell which forms like that has one face a differ 1 atom which is centered and that center atom is this one.

So, along with those 8 corner atoms, we have 2 atoms at the phase which is perpendicular to C, that means this is a C centered lattice. A different consideration of the same lattice which is drawn here in black, if I try to redraw that on this side, it encompasses a different orientation of the same lattice where the particular atom which was earlier red and the centered atom has become a body centered atom now. So, this is basically the way we look at this unit cell either we look at the unit cell like this, or we tilt the unit cell like that. The centering of the unit cell changes from C to I. Therefore, monoclinic c centered, and monoclinic I centered lattice is one and the same with a change in lattice parameter.

This particular picture is adapted from the textbook of Stout and Jensen. So, if you go and read the textbook, you will find this figure and the explanation in that. So, in association with this understanding, I would like to give you one question or a problem to all of you that in case of tetragonal lattice, we have indicated that you have only tetragonal body centered lattice or tetragonal primitive lattice. But we do not have face centered tetragonal as one of the Bravais lattice. We would like you to find out in the reason behind that.

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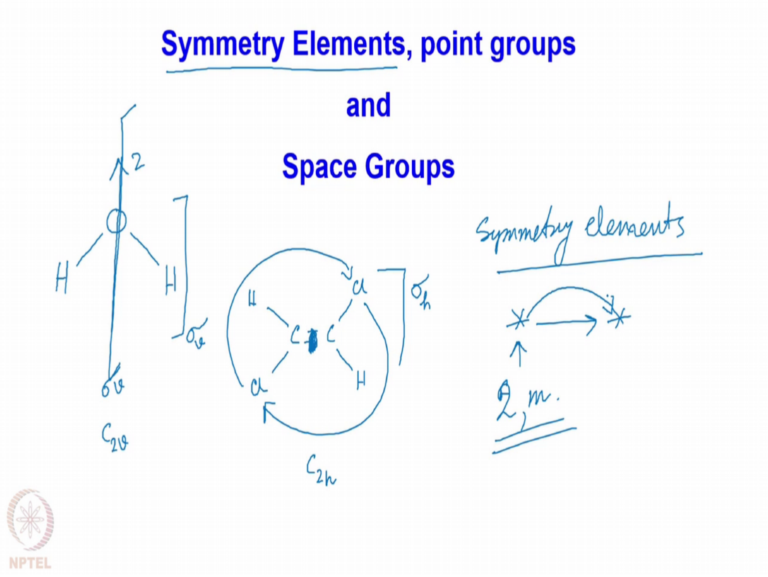

Symmetry Elements, point groups

and

Space Groups

So, now let us go in and understand the symmetry elements point groups, and space groups that are there in three-dimensional crystal structures. You must have learned about the symmetry elements in case of molecular symmetry. So, when we talk about the molecular symmetry suppose I am understand to understand what symmetry is present in this water molecule, we know that this molecule has a 2-fold symmetry, this molecule has a plane of symmetry that is the plane of the molecule. And then a mirror plane which is bisecting the molecule like this containing the 2-fold axis.

Remember both the mirror planes contain the 2-fold axis and that is why we call them as sigma vs; and the corresponding point group notation we write, as C 2 v. Similarly, if we have a molecule like this, which is 1-2 di-chloromethane; in this particular case, the 2-fold axis that is there is perpendicular to the plane of projection, so that this chloro goes to that chloro, and that chloro comes to this chloro. It is a 2-fold axis. And the plane of the molecule is the sigma plane and we write it as sigma h. So, this is molecule has point group C 2 h.

Now, in both the cases the symmetric elements that are there are within the molecule that we are talking about. So, the C 2 axis or the sigma plane it either bisects the molecule or it passes through the molecule. In case of crystallographic symmetry, the symmetry elements that we know do not go through the molecule, but rather it talks about the symmetry between one molecule, and the other molecule which is there in space. Of course in some cases, the molecule which we are talking about may have a particular symmetry say a 2fold axis or a mirror plane.

And that 2-fold or a mirror plane may coincide with the crystallographic symmetry. And we end up getting half molecule in this structure that is a special case, but in general when we are talking about symmetry in three-dimensional lattice, we are talking about symmetry between two molecules that are arranged in space following a particular symmetry.

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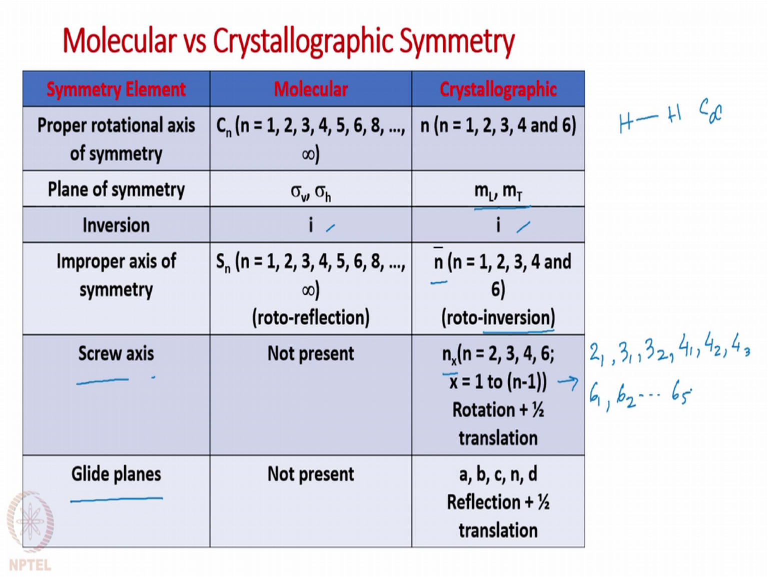

Molecular vs Crystallographic Symmetry

Symmetry Element	Molecular	Crystallographic
Proper rotational axis of symmetry	C_n (n = 1, 2, 3, 4, 5, 6, 8, ..., ∞)	n (n = 1, 2, 3, 4 and 6)
Plane of symmetry	σ_v, σ_h	m_L, m_T
Inversion	i	i
Improper axis of symmetry	S_n (n = 1, 2, 3, 4, 5, 6, 8, ..., ∞) (roto-reflection)	$\bar{n}$ (n = 1, 2, 3, 4 and 6) (roto-inversion)
Screw axis	Not present	n_x(n = 2, 3, 4, 6; x = 1 to (n-1)) $\rightarrow$ Rotation + ½ translation
Glide planes	Not present	a, b, c, n, d Reflection + ½ translation

H—H C_∞

$2_1, 3_1, 3_2, 4_1, 4_2, 4_3$

$6_1, 6_2 \cdots 6_5$

So, when we try to compare the molecular symmetry with the crystallographic symmetry, we need to understand the comparison, how these symmetry elements compare, how these symmetry elements are related, how they are different. So in case of molecular symmetry, the proper rotational axis of symmetry is identified by C n; and the n is equal to 1, 2, 3, 4, 5, 6, 8 and so on up to infinity. So, one can think of a molecule which is like hydrogen, which has C infinity axis. But in case of, crystallographic symmetry this proper axis of rotation is designated as n; and this n is nothing but 1, 2, 3, 4 and 6. We do not have 5-fold symmetry in X-ray crystallography; we do not have 5-fold symmetry in three-dimensional space lattices. We will come to that in a in a few minutes.

In case of molecular symmetry as I already indicated and you are all aware there are two types of sigma planes, sigma v and sigma h. Sigma v is the mirror plane which contains the principal axis in it. And sigma h is the mirror plane which is perpendicular to the principal axis. In this particular case of crystallographic symmetry, we have two types of mirror planes longitudinal mirror, and transverse mirror. Then in both molecular symmetry and crystallographic symmetry, we have inversion symmetry that is point of inversion I. Then in case of molecular symmetry, we have improper axis of symmetry, which is S to n, where n is equal to 1, 2, 3, 4, 5, 6, 8 whatever these are called the roto reflection axis.

Whereas, in case of crystallographic symmetry, this improper axis of symmetry becomes n bar and there also this n is 1, 2, 3, 4 and 6; and we call it as roto inversion axis. And that means, it is rotation followed by inversion. So, the difference in improper axis of symmetry and in molecular symmetry and crystallographic symmetry is in molecular symmetry, it is rotation followed by reflection. And here in case of n bar that is roto inversion, it is rotation followed by inversion.

In addition to these symmetry elements, which are common in both the systems like molecular and crystallography, we have two more symmetry elements that are coming in crystallographic symmetry. One is the screw axis, and the other one are glide planes, which are not present in molecular symmetry because of obvious reasons, because, these are not just the axis. These are rotational axis along with a translational component or a reflection with the translational component.

So, this screw axis is denoted as n x, where n can be 2, 3, 4 and 6; and x varies from 1 to n minus 1, which means if it is n equal to 2, it can be only 2, 1; in case of 3, it can be 3, 1; and 3, 2; in case of 4, it can be 4 1, 4, 2, 4, 3 and so on. So, for 6, it can be 6, 1, 6, 2 up to 6, 5. The glide planes are named as a, b, c, n and d glides. So, these bright planes are actually a reflection followed by half translation along the direction of a, b, c or n or diagonal. So, slowly we will get to know about these how the, these symmetry elements can be understood in three-dimensional.

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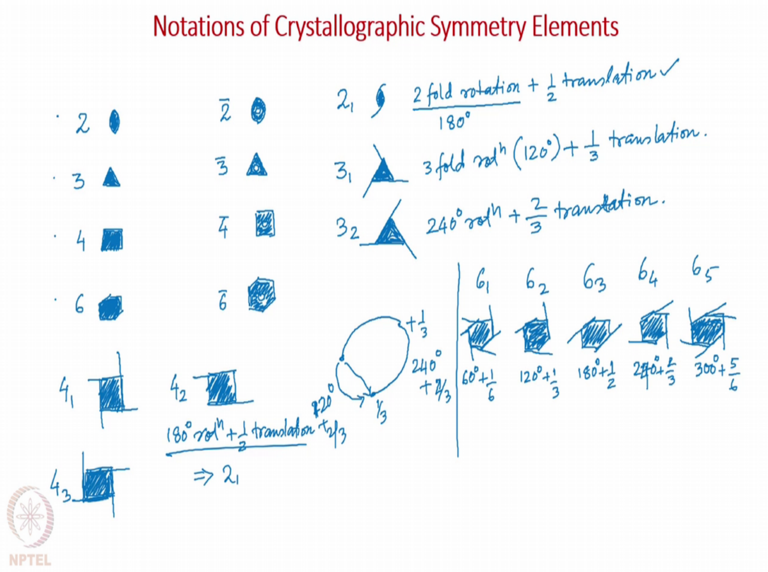

Notations of Crystallographic Symmetry Elements

So, when we have so many new symmetry elements, when we have crystallographic symmetry is identified in terms of numbers, when we try to do a projection of these symmetry elements in two-dimensional paper or any a board or somewhere, we need to identify these symmetry elements using different symbols. So, these symbols are important to identify these symmetry elements in case of, in while reading a textbook or while reading the international table of crystallography. So, the symmetry element which is the first symmetry element that we do is a 2fold axis of rotation is designated as this with a field elliptical object.

When we talk about 3fold symmetry field triangle, when we talk about a 4fold principal axis of rotation this is obviously designated as a cube as a square, which is completely filled. And a 6fold axis of rotation is designated as and as a hexagon as I am drawing here, which is also completely filled. Then simultaneously when we say 2 bar this is designated just like 2 but, with open circle in the middle, and the outer part of the circle is filled. So, this is 2 bar. 3 bar is again a triangle like 3, then you leave one open circle in the center and fill the outer part of the triangle.

Similarly, 4 bar and 6 bar also can be drawn with open circle in the middle, and the outer part of that circle is closed so, other than these as I indicated there are screw axis. So, a 2 1 screw which indicates it is a 2fold rotation, and half translation that is 2-fold rotation plus half translation that means translation along the axis, but half the length of the unit cell is a 2, 1 screw. And as you can recognize 2-fold rotation means rotation by 180 degree. 3, 1 should look like fast like 3-fold, and to indicate the translation we extent the edges like that. So, this means 3-fold rotation that means, 120degree rotation followed by one- third translation.

Similarly, the 3, 2 will be another triangle as usual. But the extension will be in the other direction indicating that the operation is taking place in the opposite direction. So, this means it is 240 degree rotation followed by two-third translations. So, what happens is in this case is the object from one point rotates by 120, but comes up upwards one-third and, then again rotate by 120 comes up by another one- third. So, from here to there directly is in opposite direction 120 degree rotation plus two-third translation, but in the current direction it is 240 degree rotation plus two-third of translation.

So, in the same manner, 4 1, 4 2, 4, 3 can be drawn like this. This is 4 1; 4 2 is interesting in one sense, because 4 2 means 180degree rotation followed by half translation which is similar to 2 1, if you look at that. And 4 3 is opposite of 4 1 as I have drawn. So, 4 1 the directions are on the left, so it is towards the right and so on. So, now the last one is 6fold, which is 6 1, 6 2, 6 3, 6 4 and 6 5. We draw it one by one. 6 1 we should have like this 6 2. We should have like that alternate edges are extended, because this is 60 degree rotation plus one-sixth translation. This one is 120 degree rotation plus one- third translation two-sixth translation means one-third translation; 6 3 means 180 degree rotation plus half translation that is three-sixth translation.

So, we should have only these two lines. 6 4, is opposite of 6 2. So, in the same manner we draw the 6, but then whatever was extended this way I extend it in the other direction and make it as 6 2, which is 270 degree rotation plus two-third translation. And 6 5 is opposite of 6 1, which is like that which actually means that it is sorry this is 2 240 degree rotation and then this is 300degree rotation plus five-sixth translation. So, as a result what is happening is by doing a rotation simultaneously moving upwards by doing it 180 degree rotation half translation another 180 degree rotation and half translation, we have translated the object from the lower unit cell to the upper unit cell.

So, that is how in case of 3 1 we start from the from one point rotated by 120 degree, but lifted by one-third, rotated by another 120 degree and lifted by another one-third rotated by another 120 degree and lifted by one-third, it comes exactly above this particular point, but it comes in the next unit cell. So, by doing this one-third, one- third up, we reach the next unit cell and that is what is the most important symmetry element in crystal structure, where a three-dimensional periodicity that is the distance between the point in one particular direction remains the same is maintained. In addition to these symmetry elements, which we have drawn here, we have other symmetry elements which we need to also know the symbols of in we know that we have mirror symmetry.

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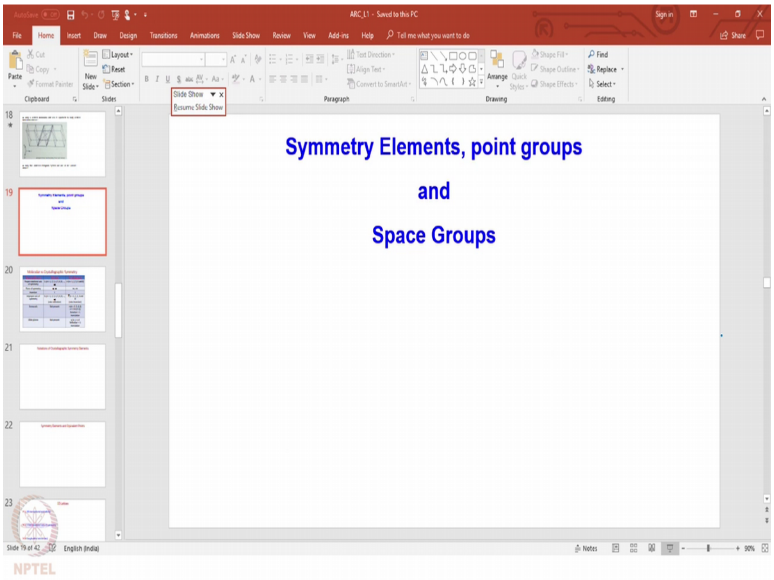

Symmetry Elements, point groups

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Space Groups

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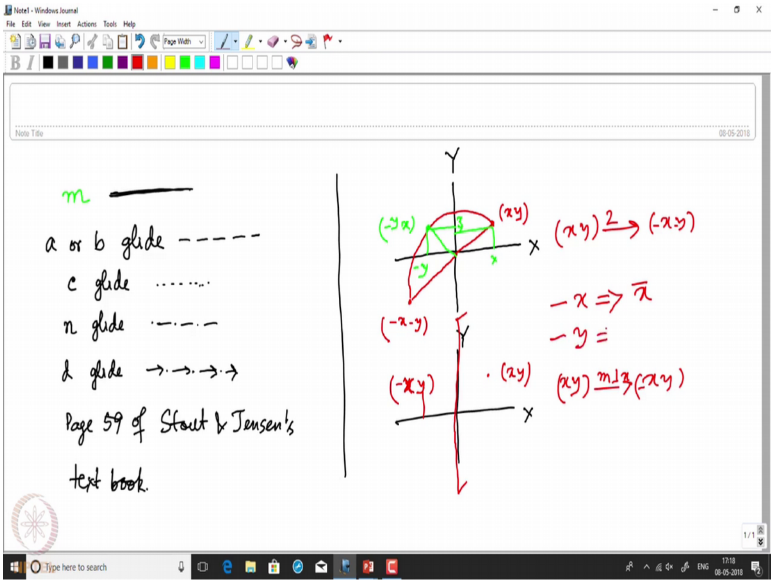

m ————

a or b glide - - - - -

c glide ....

n glide ·—·—·—

d glide →·→·→·→

Page 59 of Stout & Jensen's text book.

$(xy) \xrightarrow{2} (-x-y)$

$-x \Rightarrow \bar{x}$

$-y =$

$(xy) \xrightarrow{m \perp z} (-xy)$

This mirror plane is designated as a volt line. When you talk about a or a b glide plane, what is a glide plane, glide plane is a mirror followed by translation. So, this glide plane is designated in projection as dashed lines. The c glide is designated as a set of dots, array of dots. The n glide is designated as dot dash, dot dash, dot dash kind of notation. While the diamond glide or d glide is designated as arrow dot, arrow dot, arrow dot and so on. So, these symbols can be looked at in the page number of 59 of Stout and Jensen's textbook.

So, what happens when we have these symmetry elements, we try to identify what happens, when these symmetry elements operate to a particular point. So, to understand what happens to these points in three- dimension, we should first know what happens to a point in two-dimension. So, let us assume that we have a two-dimensional co-ordinate system where I have x and y; and in that I have a point located somewhere here, which is x y. Now, if I rotate this point by 180 degree, it comes here and becomes minus x minus y. If we rotate the point by 90 degree only, what has happens to that this intercept which was x and that intercept which was y is now changed. And this intercept here becomes minus y and this intercept becomes x. So, the point becomes y minus y and x.

So, in this way which can change the co-ordinates when we apply a symmetry. Suppose, now if I have this same co-ordinate system x and y, and we have a point in this, which is here x and y. And I am saying that I have a mirror along y perpendicular to x, where would that point come, that point would come somewhere here. And the corresponding x intercept will be minus x; and y intercept will still remain y. So, by doing a mirror x y, I am doing a mirror perpendicular to x, I am getting minus x y as the points. Similarly, here when we had x y, by doing a 2-fold, we have got minus x minus y.

So, now in crystallography, what we do is whenever we have something minus we write it as a bar. So, minus x will be written as x bar; minus y will be written as y bar and so on. So, in this half an hour lecture, we will have identified what are the different symmetry elements that we can consider in three-dimensional lattice, how they are similar, and how they are different from the molecular symmetry point of view. And we get to know, we have learned about two or more symmetry elements namely the screw axis, and glide plane.

And we know how to designate these different axis like 2-fold, 3-fold, 4-fold, 6-fold and so on, and the corresponding screw axis how what are their notations. So, in the following lecture, we will learn how to do this transformation of co-ordinates in terms of x, y, z three-dimensional coordinates. So, we will see how the equivalent points are generated when a particular symmetries of applied.