Chemical Crystallography

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

Understanding of Space Groups and Miller Indices
Lecture – 16
Miller Indices and Planar Densities

Welcome back to this course of Chemical Crystallography. I am again going to start from the last slide where we stopped in the previous lecture and I gave you one assignment to do.

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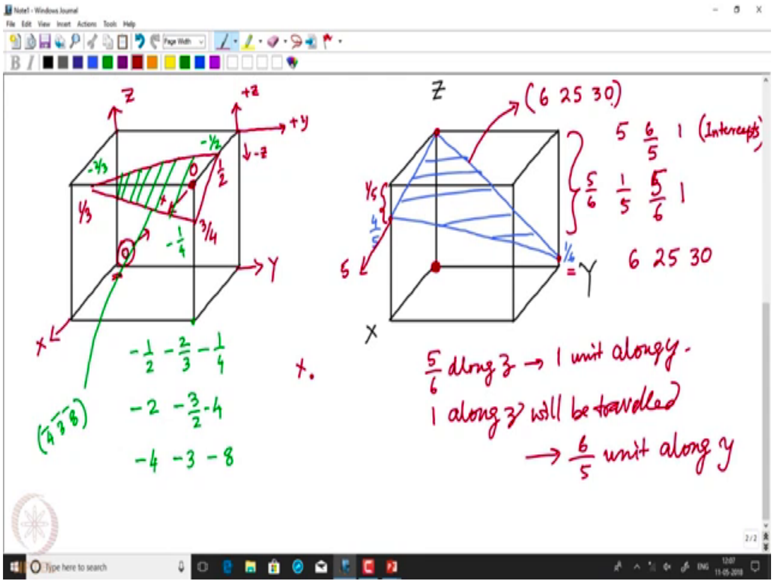

So, here we have a plane marked as blue and it has intercepts only along Z axis. So, what we should do in this case? See what has happened is when the line that we have drawn from the topmost point to this point, this is the line that is traveling along X, it has traveled one unit cell along X and it has come down from top by one-fifth unit while traveling 1 unit along X.

So, if it travels 5 such units on this side, then this will go and meet the X axis. So, the X intercept will be 5 now, on the side of Y this has traveled 1 unit along Y, but it has come down by five-sixth along Y. So, if it has come down five-sixth along z while traveling 1 unit along y at 1 along z will be traveled 1 along z will be traveled in sixth-fifth unit along y.

So, the Y intercept will be 6 by 5 and from this point the intercept on Z is 1. So, these are the actual intercepts. So, the reciprocals will be 1 by 5, 5 by 6 and 1, then you clear fractions so, multiplied by 30 so, here you get 6, 25, 30. So, the Miller indices for that particular plane become 6, 25, 30. This is to introduce that the Miller indices can be large as large as we are writing like 35, 25 and so on.

Depending on how high the resolution data is you can slice the unit cells into smaller and smaller and smaller fractions and that is where we end up getting Miller indices for different planes which are reasonably high. So, I would like you to practice these Miller indices for next few days. So, we would like now to highlight some of the general principles.

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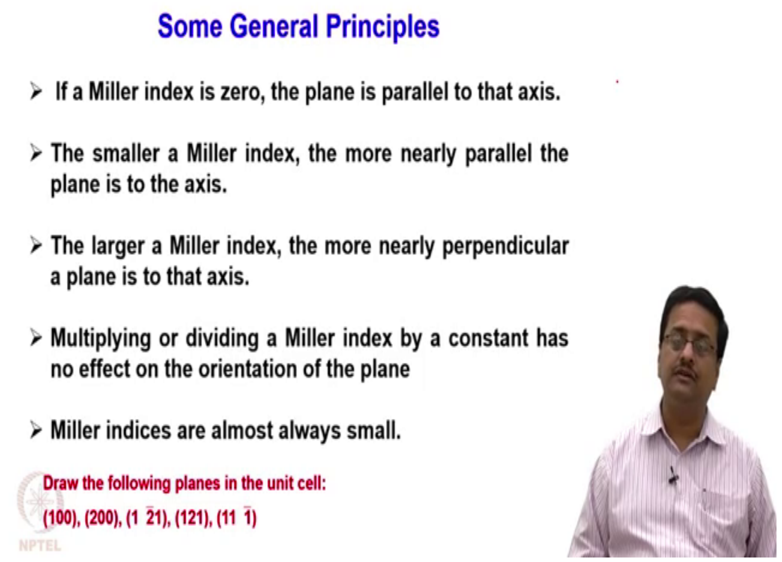

Some General Principles

- If a Miller index is zero, the plane is parallel to that axis.
- The smaller a Miller index, the more nearly parallel the plane is to the axis.
- The larger a Miller index, the more nearly perpendicular a plane is to that axis.
- Multiplying or dividing a Miller index by a constant has no effect on the orientation of the plane
- Miller indices are almost always small.

Draw the following planes in the unit cell:

(100), (200), $(1\bar{2}1)$, (121), $(11\bar{1})$

As we have already seen that if a Miller index is zero, the plane is parallel to that axis. The smaller the Miller index, the more nearly parallel the plane is to that particular axis. The larger the Miller index, the more nearly perpendicular a plane is to that particular axis. Multiplying or dividing a Miller index by a constant has no effect on the orientation of the plane, but it indicates the parallel plane.

Miller indices are almost always small for routine data because we are only worried looking at a very small fraction of the 2 theta angle that which we at which we collect the data. So, for your homework which I would like you to try to draw the different planes like 1 0 0, 2 0 0, 1 2 bar 1, 1 2 1, 1 1 1 bar kind of planes and practice drawing these different planes within the lattice within the unit cell.

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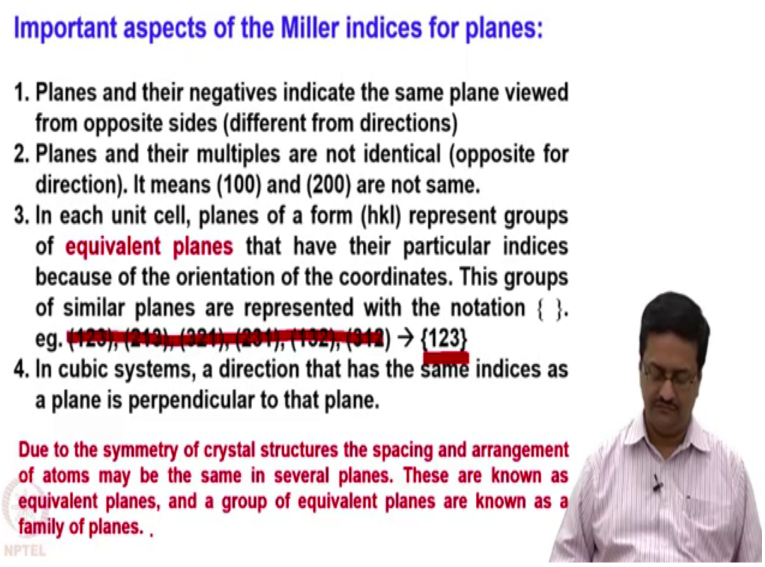

Important aspects of the Miller indices for planes:

1. Planes and their negatives indicate the same plane viewed from opposite sides (different from directions)
2. Planes and their multiples are not identical (opposite for direction). It means (100) and (200) are not same.
3. In each unit cell, planes of a form (hkl) represent groups of **equivalent planes** that have their particular indices because of the orientation of the coordinates. This groups of similar planes are represented with the notation { }. eg. ~~(123), (213), (321), (231), (132), (312~~) → {123}
4. In cubic systems, a direction that has the same indices as a plane is perpendicular to that plane.

Due to the symmetry of crystal structures the spacing and arrangement of atoms may be the same in several planes. These are known as equivalent planes, and a group of equivalent planes are known as a family of planes.

Some important aspects of the Miller indices for planes continues, the planes and their negatives indicate the same plane viewed from opposite side are different this is different for directions. So, if you have a plane h k l and you are talking about h bar k bar l bar, you are looking at the same plane from two different directions whereas, in case of crystallographic directions a plane h k l is opposite in direction compared to a peak direction h bar k bar l bar.

So, they are two opposite directions planes and their multiples are not identical; again this is opposite from that of directions which means the plane 1 0 0 and 2 0 0 are not same, but in case of direction the direction 1 0 0 and 2 0 0 indicate the same direction. In each unit cell planes of a form h k l represent groups of equivalent planes that have their particular indices because, of the orientation of the coordinates. These groups of similar planes are represented with the curly brackets.

So, these are called as family of planes as we have already indicated. So, these planes are highlighted as a family of equivalent planes 1 2 3. In cubic systems, the direction that has a direction that has the same indices as a plane is perpendicular to that particular plane.

Due to the symmetry of the crystal structure, the spacing and arrangement of the atoms may be same in several planes. These are known as equivalent planes, and the group of equivalent planes are known as family of planes.

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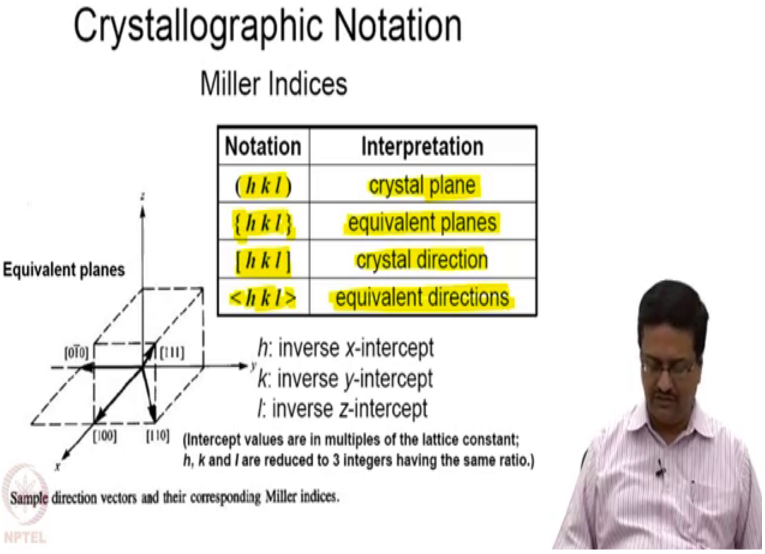

Crystallographic Notation

Miller Indices

Notation	Interpretation
(*h k l*)	crystal plane
{ *h k l* }	equivalent planes
[*h k l*]	crystal direction
< *h k l* >	equivalent directions

h: inverse *x*-intercept
k: inverse *y*-intercept
l: inverse *z*-intercept

(Intercept values are in multiples of the lattice constant; *h*, *k* and *l* are reduced to 3 integers having the same ratio.)

Equivalent planes

Sample direction vectors and their corresponding Miller indices.

So, to conclude this section, I am bringing the slight error; in that when we try to write the Miller indices when we write it using the first bracket like h k l and we do not have any comma, it indicates a crystallographic plane.

When we write h k l within the second bracket as indicated here, we are talking about equivalent planes when we are indicating the h k l within the third bracket or the square bracket, it indicates a crystal direction and when we represent h k l within this rather than less than sign, they are called the equivalent directions. So, with this, we will conclude the part where we needed to know the Miller indices for different set of planes in different crystallographic systems.

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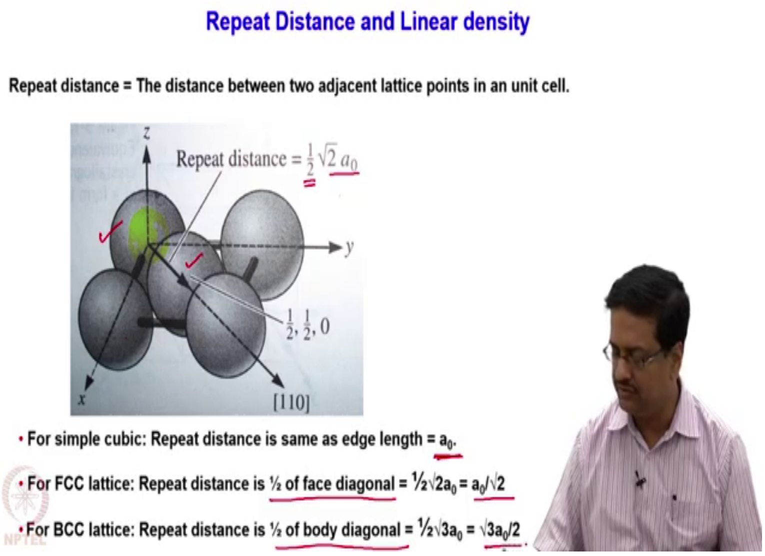

Repeat Distance and Linear density

Repeat distance = The distance between two adjacent lattice points in an unit cell.

- For simple cubic: Repeat distance is same as edge length = a_0.
- For FCC lattice: Repeat distance is ½ of face diagonal = $\frac{1}{2}\sqrt{2}a_0 = a_0/\sqrt{2}$
- For BCC lattice: Repeat distance is ½ of body diagonal = $\frac{1}{2}\sqrt{3}a_0 = \sqrt{3}a_0/2$

So, now we would like you to concentrate on and the different topic where we would like to see what are different; what are repeat distances and linear density a repeat distance means the distance between the two adjacent lattice points in the unit cell. So, in case of a face centered lattice, what we have is an atom at the center of the face and an atom at the in the figure here, what we see is that you have one atom at the center of one atom at the corner of the unit cell one atom at the center of the face.

So, the face diagonal which is a distance called root 2 a the repeat distance is half of that. So, by moving along half of this diagonal we reach one particular lattice point. So, for simple cubic that it is the repeat distance is same as a 0 for face centered lattice, it is half of the face diagonal that is a 0 by root 2 and in case of body centered lattice the repeat distance is half of the body diagonal which means half of root 3 by a 0 that is root 3 by a 0 by 2.

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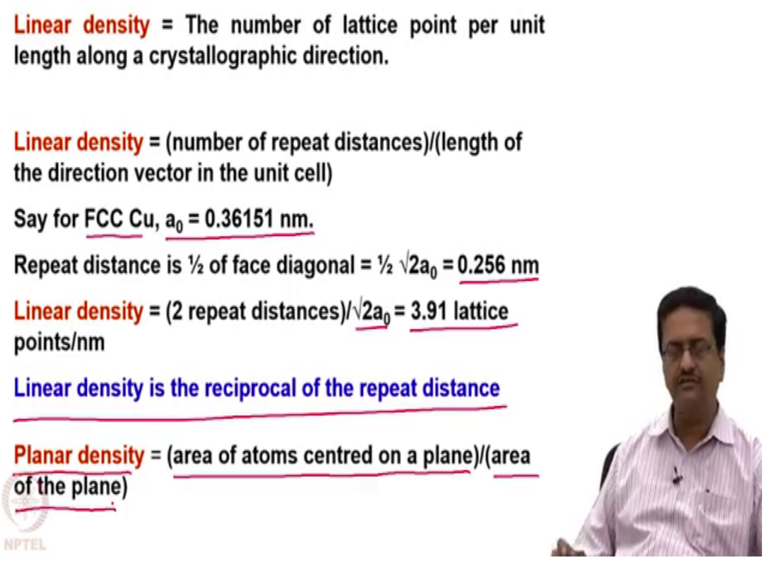

Linear density = The number of lattice point per unit length along a crystallographic direction.

Linear density = (number of repeat distances)/(length of the direction vector in the unit cell)

Say for FCC Cu, $a_0 = 0.36151$ nm.

Repeat distance is ½ of face diagonal = ½ $\sqrt{2}a_0$ = 0.256 nm

Linear density = (2 repeat distances)/$\sqrt{2}a_0$ = 3.91 lattice points/nm

Linear density is the reciprocal of the repeat distance

Planar density = (area of atoms centred on a plane)/(area of the plane)

So, the linear density is the number of lattice points per unit length along crystallographic directions. So, linear density is basically the number of repeat distance per unit length of the direction vector. So, for FCC copper when the edge length is 0.36151 nanometer the repeat distance is the phase diagonal. So, we calculated to be 0.256 nanometer.

So, the linear density is 2 repeat distances divided by the half of the body diagonal divided by the body diagonal. So, 1 point 3.91 part lattice points per nanometer and linear density is the reciprocal of repeat distance. So, similarly we can define another term called planar density which means area of atoms centered on a plane divided by the area of the plane because not all the planes will hold atoms are not all the planes will hold the center of the atoms. And then the planar density of those planes will be different from the ones where you have large number of atoms.

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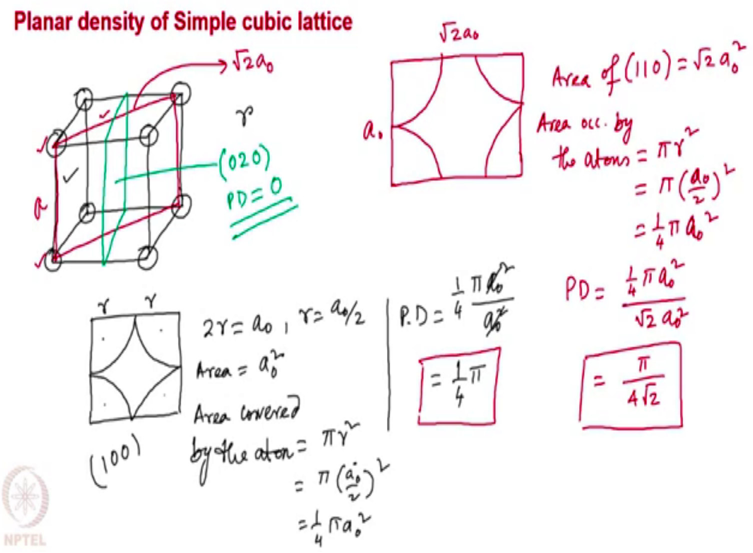
Planar density of Simple cubic lattice

So, in case of simple cubic lattice which means it is the medium that is and in that case; what we have is that the 8 corners are occupied by 8 atoms all 8 lattice points. And those 8 lattice points are such that the radius r is such that it touches the two surfaces which means if I just draw a one particular plane of the face, it should look like this.

This is the radius of the atom r; that means 2 r equal to a 0. Now for this particular face the area is a 0 square and we have one-fourth contribution from 4 atoms; that means, we have contribution from 1 atom and the area of that atom covered on that plane is the following area covered by the atoms is nothing, but pi r square because it is equivalent to one atom because a one fourth one fourth one fourth one fourth and we know r equal to a 0 by 2.

So, here we write pi a 0 by 2 square; that means, half pi a 0 square. So, the planar density for this 1 0 0 set of planes which are give faces would be the area covered by the atoms half pi a 0 squared divided by a 0 square. So, this is nothing, but equal to half pi. So, now, if I want you to determine the planar density for the 1 1 0 plane, how should we do that? We first should draw the 1 1 0 plane with the atoms placed on that along this edge which is a these two atoms are going to touch each other.

So, we write it like this, but along the face diagonal, they do not touch. So, there is a gap. Now what is the length of the face diagonal the length of the face diagonal is root 2 a or rather root 2 a 0. So, what is the area of this face area of 1 1 0 set of plane is root 2 a 0 square area occupied by the atoms equal to once again pi r square which is equal to pi a 0 by 2 square, that is ok, 1 1 mistake here, we have done is that this 2 is should be here 4. So, one fourth comes here.

So, now we do the same thing here as well. So, one fourth pi a 0 squared. So, the corresponding planar density will be one fourth pi a 0 square divided by root 2 a 0 square which means pi by 4 root 2. So, now, we see that the planar density of 1 0 0 plane and 1 1 0 plane are different; what will be the planar density of this particular plane. What I what are the Miller indices for this plane the Miller indices for that plane is 0 2 0, you see here in this plane, we do not have any atom centers located; that means, no atom has contribution on this plane, if we consider hard sphere. So, the planar density is going to be 0.

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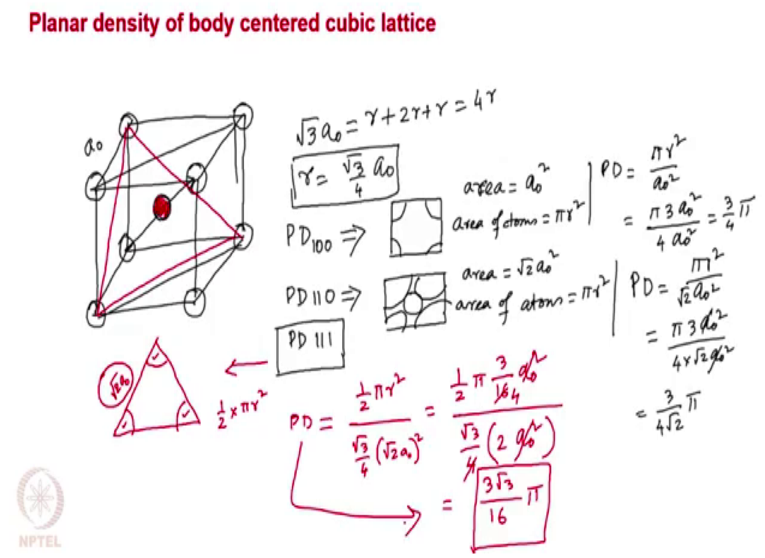

Planar density of body centered cubic lattice

Now, let us see the planar densities of various planes on body centered cubic lattice in case of body centered cubic lattice, we have atoms at 8 corners and the atom is located at centre of the unit cell in case of body centered lattice what is the closed pack direction the closed pack direction is the body diagonal. So, if the edge length is a 0 the body diagonal is root 3 a 0 which is equal to r 2 r plus r which is equal to 4 r. So, r equal to root 3 by 4 a 0.

So, now if we try to determine the planar density of 1 0 0 planar density of 1 1 0 and then planar density of 1 1 1, we should follow the same procedure as we have done before, we should first draw the plane and in this case since the body diagonal is the closed packed direction the atoms do not touch along the edge. So, we should draw it like this the area of this surface is nothing, but a 0 square area of atoms is nothing, but pi r square. So, the planar density is equal to pi r square by a 0 square, but now r is equal to root 3 by a 0 root 3 by 4 a 0. So, pi 3 a 0 square by 4 a 0 square which is equal to 3 fourth of pi 1 1 0 that is the plane which is here. So, the plane 1 1 0 would have the atoms touched along the corner like this.

So, again the area of that plane is root 2 a 0 square area of atoms is pi r square. So, the planar density should turn out to be pi r square divided by a 0 square and now sorry root 2 a 0 square. So, now it is pi 3 a 0 square by 4 into root 2 a 0 square. So, it is equal to 3 by 4 root 2 pi now the point is going to be interesting for planar density of 1 1 1 although this although this body center atom which is at half is located at the center of the unit cell.

This atom does not have it centered on the 1 1 1 plane, it does not lie on that 1 1 1 plane, it is the other lies slightly above the 1 1 1 plane. So, when we try to draw this 1 1 1 plane, we should draw it as a triangle and then the 3 atoms at 3 corners should come like that. So, now, the body this face diagonal is root 2 a and I have one-third one-third rather one-sixth one-sixth; one-sixth; that means, half of the atom located on this. So, half into pi r square is the occupied area and this is the side a edge length of this equilateral triangle. So, the planar density that one should calculate is 1 by 2 pi r square divided by root 3 by 4 root 2 a 0 square. So, now, half pi r is root 3 by 4; so, 3 by 16 a 0 square and root 3 by 4 2 a 0 square.

So, a 0 square is cancelled 4 this cancelled here. So, here what we get is 3 root 3 by 16 pi. So, this is the planar density for the 1 1 1 plane in body centered cubic lattice. So, today we have seen how to identify the h k ls for crystallographic planes and we have learnt about the linear density and planar density. Then in the next class, we will continue in this direction and we will see how these planar densities can be utilized to identify the strength of those diffractions from different crystallographic planes.

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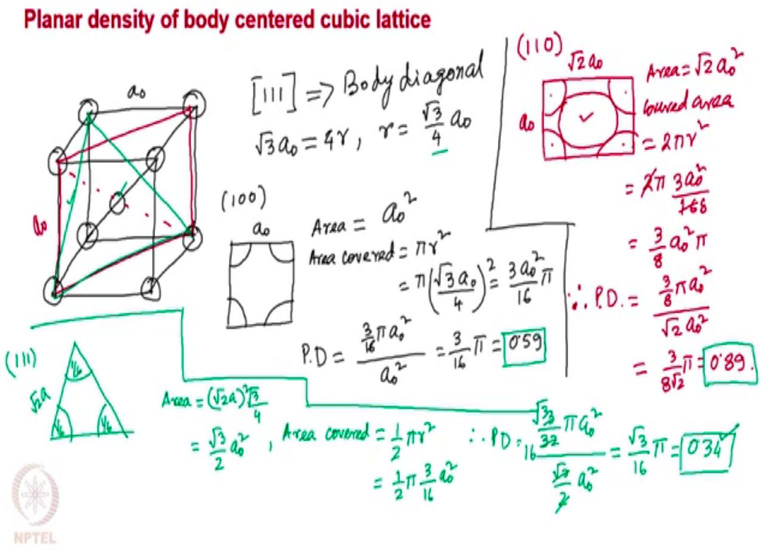

Planar density of body centered cubic lattice

Now, let us try to work out the planar density of body centered cubic lattice and we will try to see how the planar density changes for different planes like 1 0 0, 1 1 0 and 1 1 1 planes. So, let us first draw the body centered lattice as you know the body centered lattice has 8 lattice points at 8 corners and a lattice point at half half half. So, we have atoms at 8 corners and at the center of the lattice.

So, in case of body centered lattice, the closed pack direction is the 1 1 1 direction that is the body diagonal. So, if the edge length is a or a 0 the body diagonal is root 3 a 0 and it is close packed along the body diagonal. So, when we connect corner to corner, we pass through 2 atoms. So, the diameter of two atoms is incorporated here. So, the length in terms of atomic radius is 4 r which means r equal to root 3 by 4 a 0.

So, now, with this in mind let us start working out the 1 0 0 plane the 1 0 0 plane is the face one of those 6 faces of a cube and remember since the body diagonal is the closed packed direction the atoms do not touch along the face the edge length of for the face is a 0. So, the area of each face is a 0 square and the area covered by the atoms is nothing, but pi r square because one fourth, one fourth, one fourth and one fourth gives you pi r square which is equal to pi r square is root 3 a 0 by 4 whole square which is equal to 3 a 0 square by 16 pi.

So, now the corresponding planar density turns out to be 3 by 16 pi a 0 square divided by a 0 square which is equal to 3 by 16 pi which is equal to 0.59. Now if we do it for the other plane which I told is the 1 1 0 plane the 1 1 0 plane is the plane which I am drawing in red. So, in this plane, we have a body diagonal connecting the other corners. So, if we try to draw the 1 1 0 plane in case of body centered cubic lattice, we would have 4 atoms at 4 corners and the central atom would touch the 4 corner atoms along the body. So, the edge one of the edge is a 0 which is this one, but the other edge is the face diagonal which is root 2 a 0. So, the area that it encompasses is root 2 a 0 square.

Now, inside this area you have for one fourth portions of the atom and one full atom; that means, total two atomic area is covered in this 1 1 0 plane of body centered lattice. So, covered area is nothing, but 2 pi r square. So, this 2 pi r square can be written as 2 pi 3 a 0 square by 16 which means it is equal to 3 by 8 a 0 square pi therefore, the planar density could be 3 by 8 pi a 0 square divided by root 2 a 0 square.

So, this value would turn out to be 3 by 8 root 2 pi which is equal to 0.89. So, now, let us see what happens if we try to do the same for the plane 1 1 1. Now you see that interestingly, this 1 1 1 plane does not contain that point which is at half of half. So, the 1 1 1 plane which is a triangular plane should look like this where we have 3 coordinates occupied by the atoms and the every side is corresponding to root 2 a.

So, the area under this triangle is nothing, but root 2 a square root 3 by 4 which means it is equal to root 3 by 2 a 0 square. Now the area covered is equal to one sixth; one sixth; one sixth; that means, 3 parts of one-sixth means half pi r square what is r r is equal to root 3 by 4 a 0. So, a square is 3 by 16 a 0 square; that means, the planar density is equal to the planar density is equal to 3 by 32 pi a 0 square divided by root 3 by 2 a 0 square.

So, you can work it out. So, it is equal to root 3 by 16 pi which means that the value turns out to be 0.34 a very small number. So, this indicates that in case of body centered lattice the plane 1 1 0 has much higher planar density compared to that of the 1 1 1 plane and the face the plane which corresponds to the face which is 1 0 0 plane has an intermediate density. So, in this lecture, we have learned how to calculate the linear density and planar density of different systems.

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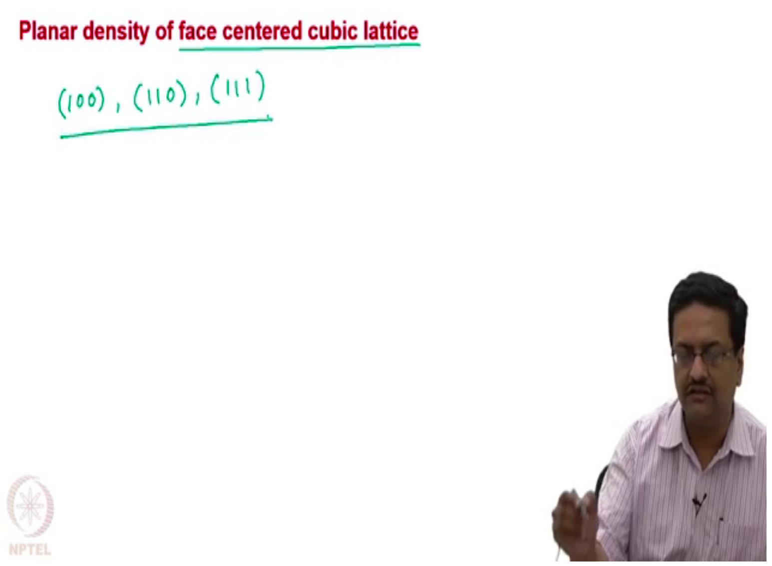

Planar density of face centered cubic lattice

(100), (110), (111)

So, what I would like you to do yourself is to calculate the planar density of face centered cubic lattice for the planes 1 0 0, 1 1 0 and 1 1 1 and compare their values yourself.