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

Lecture - 61
Ewald's Sphere and Limiting Sphere

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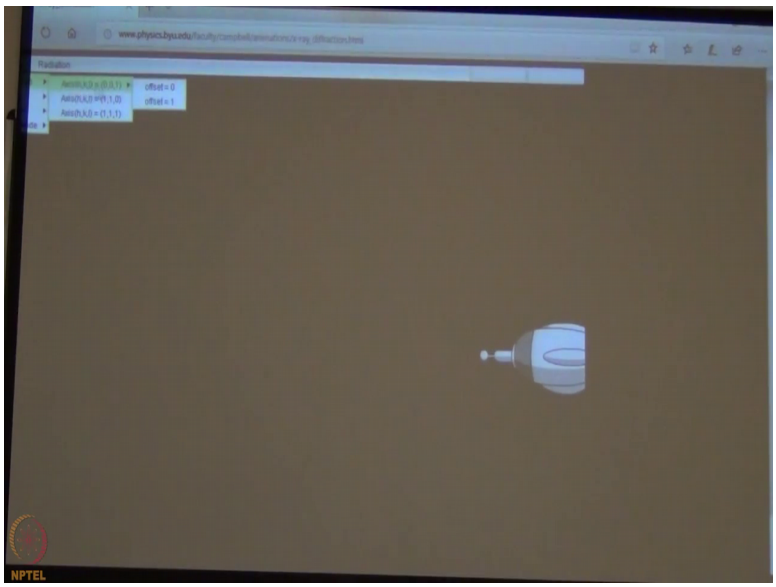

What you are seeing is: this end is at particular point is your source. So now, I am choosing radar crystal and it is about one particular axis is oriented.

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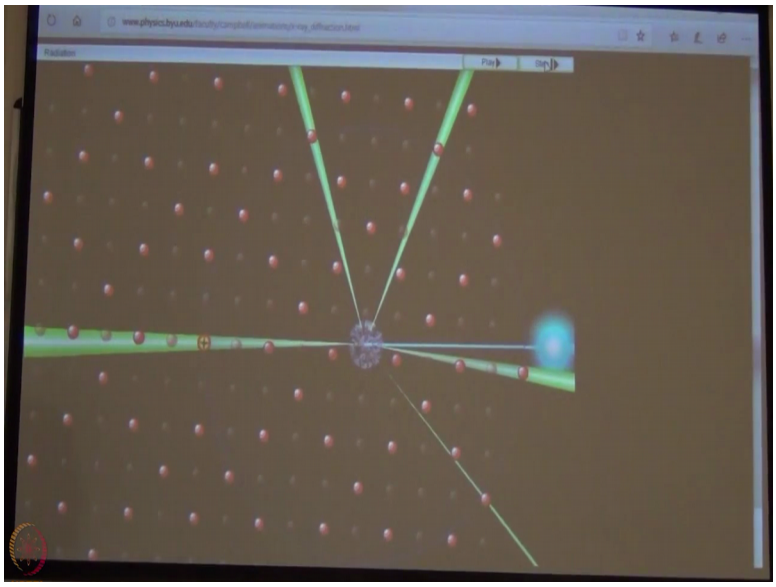

So, now that is the position of the crystal, this is the source. And then there is one change blue circle that is your Ewald's sphere of sphere of reflection. So now, you can see these points some of them are bright and some of them are dull; I will explain you why some are bright and some are dull. Those points are the corresponding reciprocal lattice points of this particular crystal in a given reciprocal lattice plane. Crystal is oriented in one direction so it says it is 001 plane of reciprocal lattice.

So, now you see when a particular point is crossing the reciprocal lattice this you are sphere it is diffracting. This point is exactly the straight line from the beam and this beam is enormously intense. So, when we learn the when we discuss about X-ray diffractometers we will get to know we do not use anything which is with will go straight. So, what we do is we use a beam stop the piece of length to stop the direct beam from falling on the detector the static beam is very intense.

And detector is sometime placed in such a way that the direct beam can go and keep that it. So, we place a very small piece of led just behind the crystal to stop anything wasted so that is where that is across. But you see now, if I start the video see whenever a reciprocal lattice find is crossing the blue sphere it gives you diffract. And if you try to see keep your eye fixed on suppose this dull spot and see what happens and in this step also.

See now the dull spot enters the Ewald's sphere and goes and does not cause difference right. If you keep eye on that right spot that right spot right. Reciprocal lattice point as soon as it touches the reflection starts two three steps. You get the maximum intensity and when it goes inside the intensity database. So, what all steps I have done are snapshots of diffraction image of this crystal.

I am rotating the crystal maybe every time by 0.1 degree or 0.2 degree or 0.3 degree. The reciprocal lattice one slowly moves in space. So, at one point when it just touches the circumference of the sphere of radius 1 by lambda it starts to diffract. It may take 3 or 4 frames of 0.3 degree width for that reflection do pass through the circumference. So, in 1 2 3 or 4 frames you will have same spot, starting with a very small intensity next one with her slightly higher intensity, third one we have a slow intensity, fourth one very low, fifth one almost nothing, and six ones in 0.

So, if you try to measure the intensity in terms of electrons and then you plot number of electrons versus angle of rotation you will if you get a Gaussian type of curve. Sometimes some reflections are very sharp and very high intensity it may. So, happen that in one frame it is very small second frame it is anonymously large and third frame it has disappeared that also is possible. So, that is why we always try to record X-ray diffraction data with a very very small width.

Width means; the angle by which you rotate the crystal either you rotate it by its own axis which is call phi or you keep the crystal like this and rotate it like that which is omega normally we 2 phi and omega scans. But then it is possible to keep the crystal exactly particle or exactly horizontal the angle the crystal makes with the horizontal plane is called kappa. So, three different angles about which one can orient the crystal two different angles about which one can rotate the crystal. And the third angle which is the fourth angle which is 2 theta is the position of the detector that also can be changed.

Suppose, if you have placed your detector somewhere here; exactly the place wherever put my hand if you have put the detector here. You are technically covering from about 0 degree to about 55-60 degree in 2 theta. So, anything comes from here up to this is going to detector this detector is not going to record this on that or that reflection. So, in the position of the detector at about say 30 degree with respect to the beam the covers from 0 to 60 degree. Center of the detector is an about 30 degree with respect the beam.

If you place the detector like this straight along the direction of the beam you get plus plus in minus side. So, on either side your maximum 2 theta is 90 degree, but then if you have a put as chance to get the detector somewhere there. When that this angle is maybe 90 degree this angle may be 90 degree here this one there you may not from here to here. So, you we replace the detector at higher value of theta you record diffraction data that is going at will higher.

What is going on very high angle? The reciprocal lattice points which correspond to very very small d values. Very small d value means very large 1 by d; that means, it is further away from your sphere. So, if we go back to this presentation I mean I can then explain the ones which are further away crosses the Ewald's sphere at further angle with respect to the crystal. So now, you see here some of the spots are dark and some are not.

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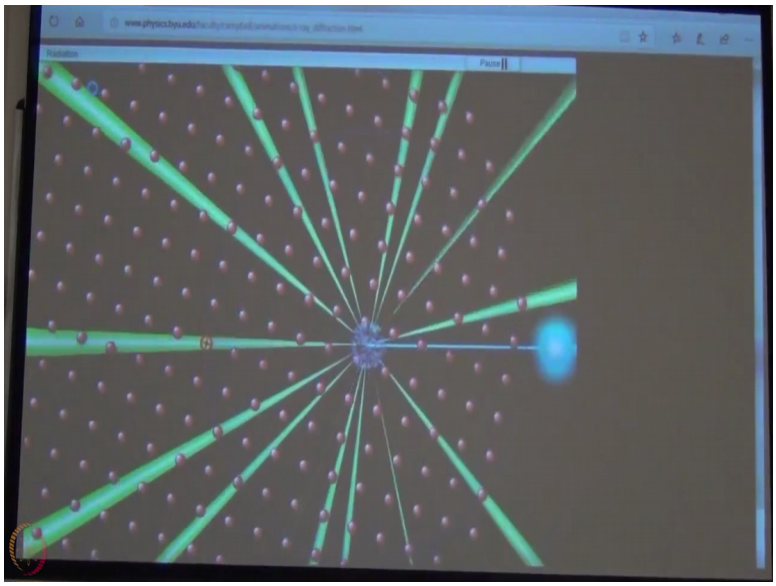

I change it to some other crystal you see all of different lengths right. There is no dark spot and all the spots which are there whenever they are crossing that blue circle is making difference.

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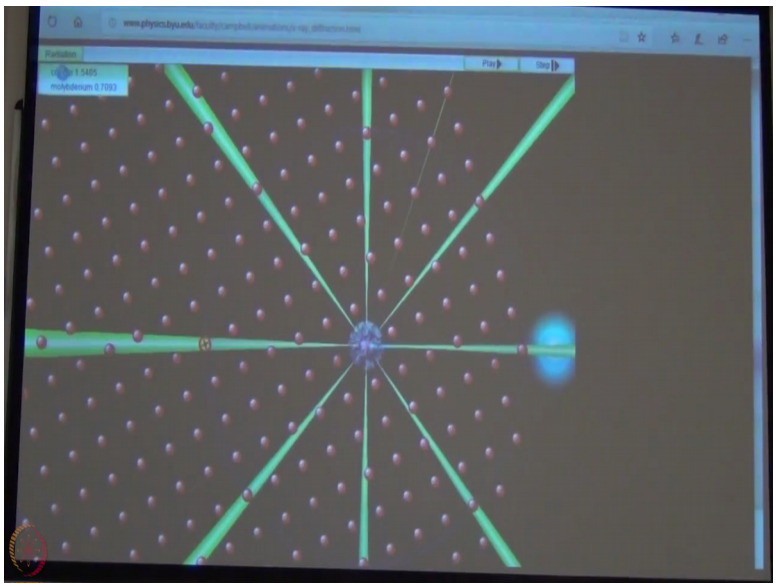

Now, I change the radiation, it was done using molybdenum till now.

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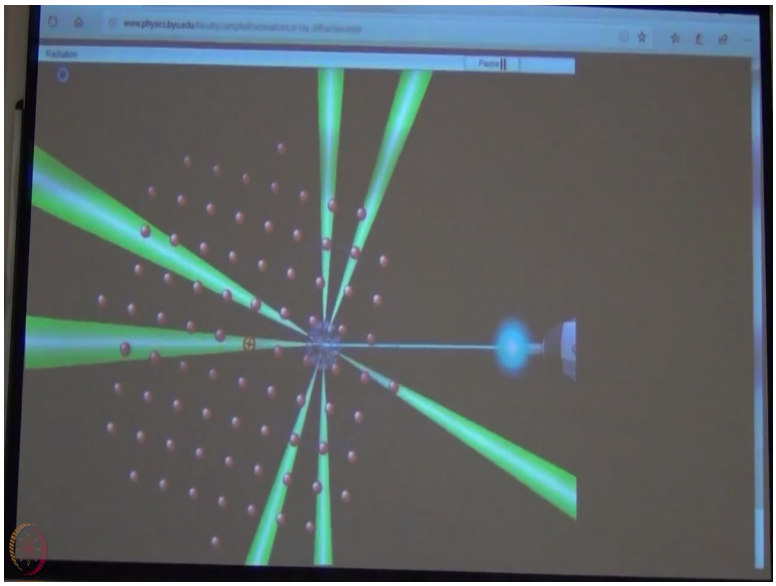

I changed it to copper, for copper that blue circle is smaller because, red length is larger. So, 2 by lambda is the sphere which is like this. So, the number of spots that can be accessed has drastically reduced compared to molecular here. So, here again if I go back to diagonal crystal and one particular thing one particular plane the same situation is there some bright and some dull spots. But the number of spots the number of reciprocal lattice points that you are seeing is much much less compared to what you would get if you just change it from copper to molecular right. Do you know why this is seen, what is the reason behind it.

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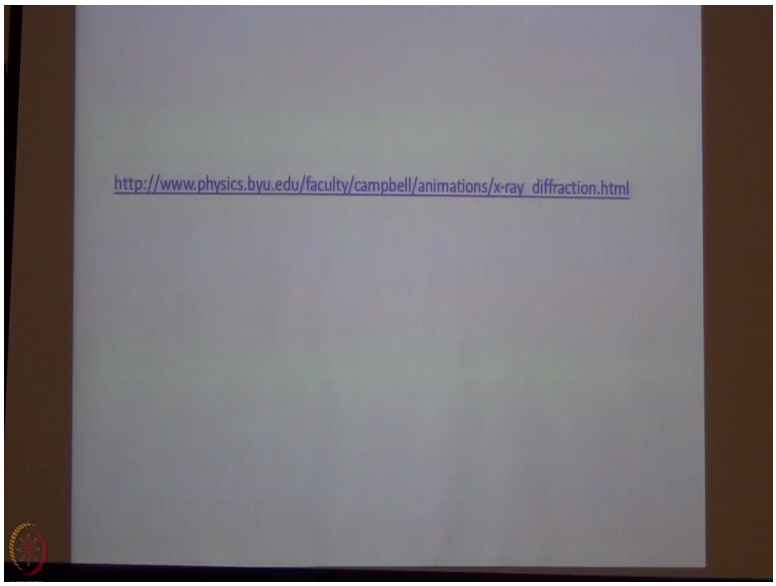

Can somebody guess the reason behind that?

Student: Interference.

Interference, what kind of interference?

Student: Both constructive and destructive.

Constructive interference gives you deflection destructive interference does not give you deflection. So, there are some set of frames or which there is always destructive interference. And for some setup planes there is always constructive interference nothing in between so that is called the systematic absence. So, before I go to that.

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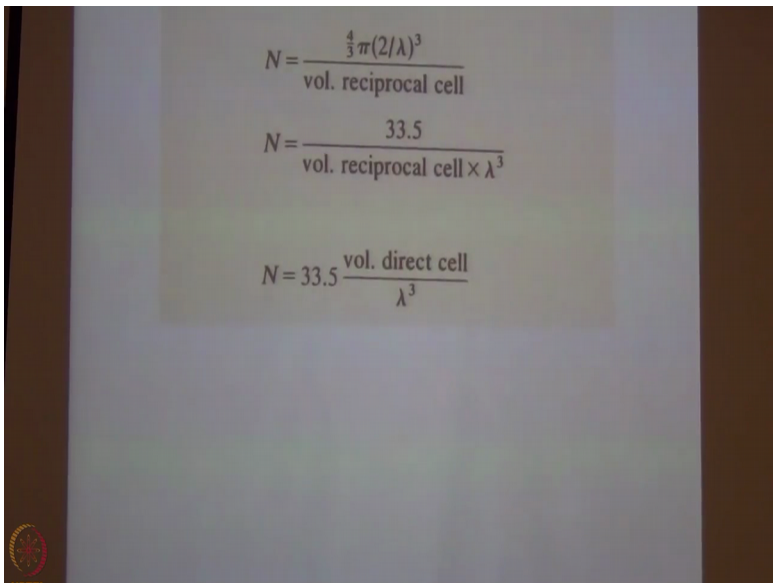

So, this is the very simple formula, to calculate the total number of reflections N that one can achieve using a particular wavelength lambda for a particular crystal of a given 1. You see it probably depends on 2 by lambda, 2 by lambda is what? Diameter of the Ewald's sphere. So, the number of spots that can fall inside the Ewald's sphere is the volume of Ewald's sphere divided by volume of reciprocal lattice. So, when you simplify this N is equal to volume of direct lattice by lambda cube with the multiplication factor of 33.5.

So now you see molybdenum radiation one can calculate what could be the maximum number of achievable reflections. And this maximum number of achievable reflection

means the maximum resolution that one can achieve with molybdenum radiation. Not restricted with 2 theta up to which you can collect data the maximum resolution that one can achieve with molybdenum is 0.71 by 2 angstrom. But we do not go to that, but this number gives you the maximum number of accessible reflections.

And if you do it for a given cell; suppose if you just take this as 1000 cubic angstrom. Do it for copper and molybdenum we will see there is a drastic difference, because in one case it is 1.54 cube in one case it is 0.71 cube. 0.71 cube makes the number much much smaller 1.5 for cube makes this number larger. As a result the division is giving you a much less number of reflections with copper compatibility. So, now we just want to go to that systematic absence.

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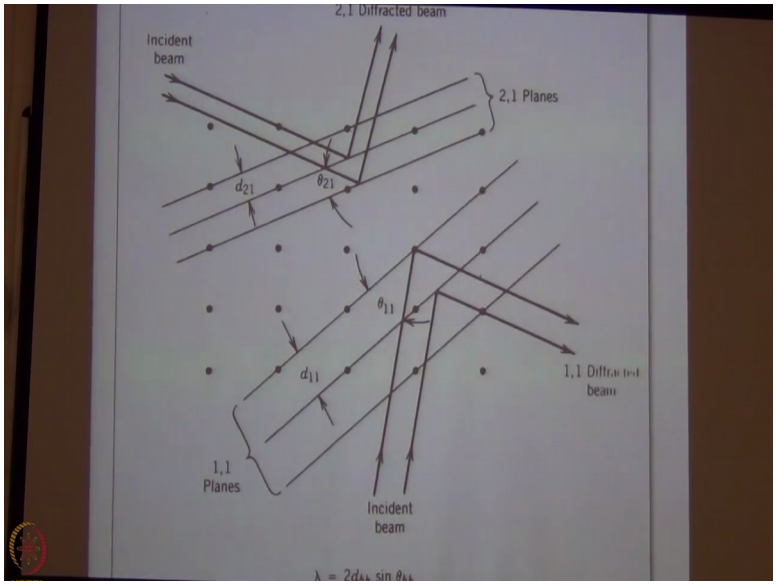

If you look at this area of points, this area of point has arrangement of the primitive lattice. If you construct an unit cell do not want into drop you now all of these are where in your stop dimension I have taken the figures from there I leave the topic today. These points correspond to primitive lines suppose it is in 2 d. So, if you join the corner points and draw the plane these are 1 1 planes right.

These are 1 1 plane and governs which are drawn here I am joining this corner to the corner of next units. That means, it is passing through the midpoint of this axis so it becomes 2 1 set up. So now, you see these 2 1 set of planes are different from 1 1 set of planes and in between the 2 1 set of planes there is no other plane. In between the 1 1 set

of planes we do not have any other. So, in case of primitive lattice we will get diffractions from both the sets of planes.

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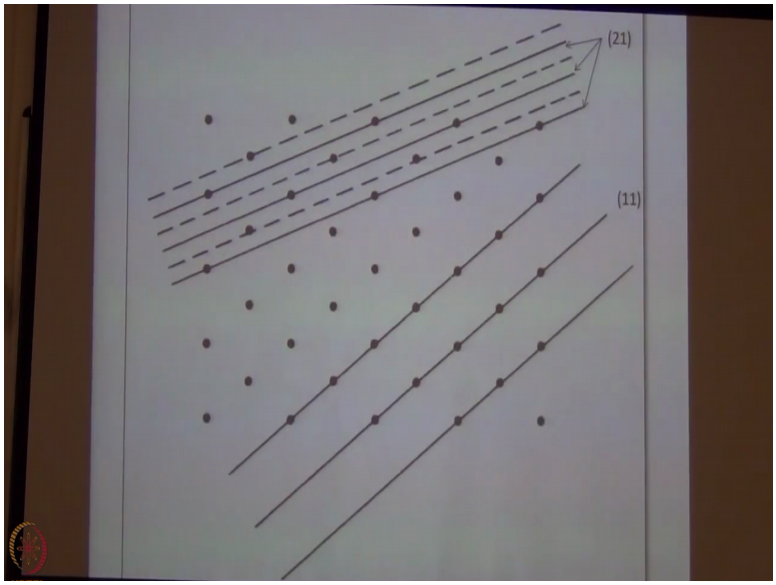

If I now change it to a centered lattice if you just look at this point 1 2 3 4 you have a center point 1 2 3 4 you have a center point. So, now I am draw it 1 1 set of planes. So, drawing 1 1 set here wings I am joining the corners knowing that is no framing between so it will be Braggs condition. Look at the 2 1 set of planes start here from there I am passing through the midpoint of that axis I am going to the next. So, this is a commandment basically a 2 1 plane is from here going through that.

If you consider this as your unit cell this is the second lattice point if you go there. So, these dark lines are to one set of planes. Now, who told you that those are corner points and these are center points. And then you know I will take those as my corner points and data center point. So, if I do so this is my lattice so I draw when 2 1 plane from here bisecting that axis and going there. So, the dash line is also 2 1 set of planes. So, the distance between two parallel dark lines is d 2 1 distance between two dash line is also d 2 1.

But, they are same in terms of electron basis if you see the atomic disposition in the dash lines and the bolt lines they are identical. That means these two are same set of planes with half distance. If Bragg condition is valid for d 2 1 it will not be valid for half of it will not be satisfying transfer. So, in this case in the center lattice now will be destructive

interference of thing of diffraction. And systematically all through 1 set of reflections will be offset. So, 1 1 is there or 2 1 is us what is the origin of this systematic absence, what do you what do you think, why we suddenly encountered systematic absence condition for it centered lattice which was both their intensity.

A C centered lattice has an additional translational symmetry which is different from a lattice translation. The lattice translation is one unit translation from this room to that room from here to up, but this involves half lattice translation. This point is translated here by half along x and half along y. So, this non lattice translational symmetry is responsible for the origin of systematic absence. Can you tell me then, what are these symmetry elements that will give you systematic absence.

Student: (Refer Time: 19:42).

Right next.

Student: (Refer Time: 19:45).

Through axis and if it is a centered lattice then it is face centered lattice, body centered lattice. What in case of monoclinic c centered lattice all we have some of the other systematic absence condition. Now look at this if it is 2 1 there is a systematic absence what about 2 2 what about 2 2 think about it there. When it is 2 2; that means, it is copying here half and they are half wavelength that in between.

And there is no other plane which will have same atomic disposition or no atomic disposition are to do. It will not be systematically absent, but it may have a very low intensity. Low atomic centered on that plane up to do so it will have a low intensity. But it will not be absent because there is no other plane in between 2 2 2 planes having the same disposition. So, when I say h k l he has odd the systematic absence.

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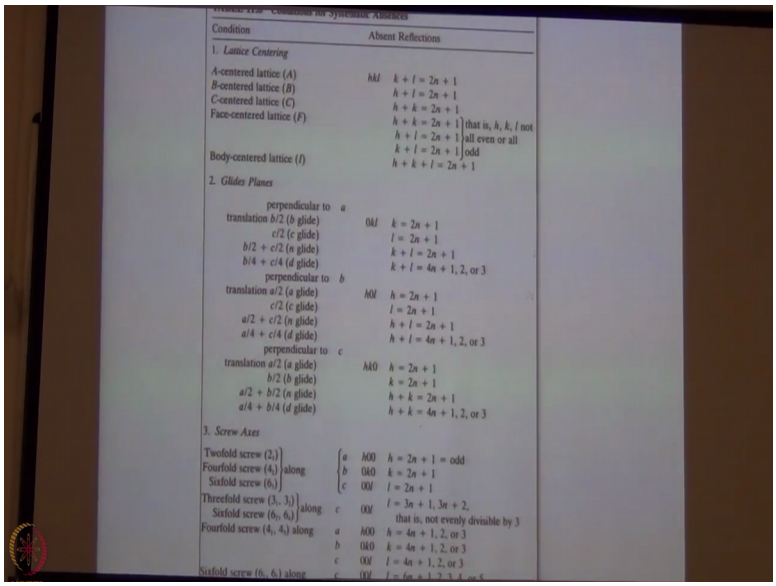

Condition		Absent Reflections	
1. *Lattice Centering*			
A-centered lattice (*A*)		*hkl*	$k + l = 2n + 1$
B-centered lattice (*B*)			$h + l = 2n + 1$
C-centered lattice (*C*)			$h + k = 2n + 1$
Face-centered lattice (*F*)			$h + k = 2n + 1$ | that is, h, k, l not
			$h + l = 2n + 1$ | all even or all
			$k + l = 2n + 1$ | odd
Body-centered lattice (*I*)			$h + k + l = 2n + 1$
2. *Glides Planes*			
perpendicular to	*a*		
translation *b*/2 (*b* glide)		*0kl*	$k = 2n + 1$
c/2 (*c* glide)			$l = 2n + 1$
b/2 + *c*/2 (*n* glide)			$k + l = 2n + 1$
b/4 + *c*/4 (*d* glide)			$k + l = 4n + 1, 2, \text{or } 3$
perpendicular to	*b*		
translation *a*/2 (*a* glide)		*h0l*	$h = 2n + 1$
c/2 (*c* glide)			$l = 2n + 1$
a/2 + *c*/2 (*n* glide)			$h + l = 2n + 1$
a/4 + *c*/4 (*d* glide)			$h + l = 4n + 1, 2, \text{or } 3$
perpendicular to	*c*		
translation *a*/2 (*a* glide)		*hk0*	$h = 2n + 1$
b/2 (*b* glide)			$k = 2n + 1$
a/2 + *b*/2 (*n* glide)			$h + k = 2n + 1$
a/4 + *b*/4 (*d* glide)			$h + k = 4n + 1, 2, \text{or } 3$
3. *Screw Axes*			
Twofold screw (2_1) | Fourfold screw (4_2) | Sixfold screw (6_3)	along	*a*	*h*00 $h = 2n + 1 = \text{odd}$
		b	0*k*0 $k = 2n + 1$
		c	00*l* $l = 2n + 1$
Threefold screw (3_1, 3_2) | Sixfold screw (6_1, 6_5)	along	*c*	00*l* $l = 3n + 1, 3n + 2,$ that is, not evenly divisible by 3
Fourfold screw (4_1, 4_3)	along	*a*	*h*00 $h = 4n + 1, 2, \text{or } 3$
		b	0*k*0 $k = 4n + 1, 2, \text{or } 3$
		c	00*l* $l = 4n + 1, 2, \text{or } 3$
Sixfold screw (6_1, 6_5)	along	*c*	00*l* $l = 6n + 1, 2, 3, 4, \text{or } 5$

So, this is a base which if you do not understand you will have to memorize and if you understand you do not have to understand. At some point was the middle of this course we will be able to derive these conditions using some mathematical to, but for the time being we can try to understand their physical. So, I am it is lattice centering when I say A B or C one face is centered one face is centered the centering is giving you one lattice translation along a particular face.

And that particular face is designated by h plus k or h plus l or k plus l. So, when it is suppose c center; that means, a b face centered c centered means the face a b is centered. So, when it is A Bit is h plus k which is odd, when it is B centered; that means it is A C face. A and C means h and l c h plus l is odd because the translation is along in this case it is along A and B, this case it is along A and C, in this case it is along B and C. So, that is how for general reflections h k l A plus l odd represents a centered h plus N odd represents b centered and h plus k odd represents c centered.

Immediately explained it to face centered cubic or face centered lattice. What does a centered lattice means, all the face center so simultaneously all those three conditions will have to be revalid. So, for a face center lattice all the reflections which satisfies one of those three conditions will be cause systematically absent. So, far as simply give it to face centered lattice a large number of reflections will be half center due to symmetry of symmetry of face centered. For body centered lattice the translation is related in all the

three directions it is half half half. So, from there to there I am doing a translation half half half.

So, the motion of that atom is in all the three direction So, when the condition becomes h plus k plus l the sum is odd. So, in case of what a centered lattice if it is 1 1 1 plane 1 plus 1 plus 1 3 or 1 0 0 or 1 2 0 startup right; so you can understand quickly decide looking at the h k l values whether it is primitive or body center or face center or one face center now somebody said glide planes. What does a glide plane do it is a reflection followed by translation; translation is along one axis reflection is perpendicular to the plane.

So, now if I think that a glide plane which is perpendicular to a immediately that index becomes 0. Any glide which is perpendicular to h the reflections which are having 0 k l set of reflections will suffer. Now this, a glide for get a glide perpendicular to a can be B glide or C glide. So, B glide perpendicular to a means translation is along B.

So, in set of 0 k 0 0 k l set of reflections k odd will be absent; if it is a B glide perpendicular, B glide this translation along B. So, the mirror index which corresponds to B will be odd for systematic absence; C glide perpendicular to a means translation along C. So, 0 k l set of deflection k will be on not k and then corresponding N glide it is k plus l N glide means.

Student: translation (Refer Time: 26:39).

Translation along both B and C; so k plus l is on what is a di 1 glide di 1 glide is one fourth translation. Then the systematic absence condition is like four N plus 1 2 or 3 all of which leads to odd number that is 4 N plus 1 2 or 3. So, similarly perpendicular to B and C can be rig ht when you go to screw axis. It is 1 axis so if it is along B x and y change it is sign, x y z becomes minus x y z. That is why the reflections which are affected are h 0 0 0 k 0 and 0 0 l. Because here it means mirror case x y z mirror perpendicular to B makes it x y bar z y becomes y bar.

So, that we say that it is h 0 l; similarly the ones which change sign which a make those indices to 0 because those are not vary. What is vary it is the translation. So, screw axis 2 1 parallel to a means h 0 0 set of reflections are to be looked at and we will look for h two fold form.

So, if we see that 1 0 0, 3 0 0, 5 0 0 7 0 0, 9 0 0 all these three planes are absent. It is conclusion that it is a 2 1 screw along it 2 1 is equivalent to 4 2 is equivalent to 6 3. So, similarly 3 1 6 1 and all that, you have different systematic absent conditions this systematic absence conditions are again telling you can be derived mathematically we will do it at some point.

And these systematic absence conditions are absolutely required for determination of space group see when we collect a crystal data; we collected based on the lattice parameters A B and C with alpha beta gamma, and then at some point if you have sufficient number of reflections at the beginning of your data collection. You may be able to see some of those systematic absence conditions; those are applied on general reflection h k l those are not applied on some special types of reflections and in your special indices.

So, it is easy to observe those compared to these.