Symmetry and Structure in the Solid State

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Lecture – 37
Bragg's Law in Reciprocal Space 2

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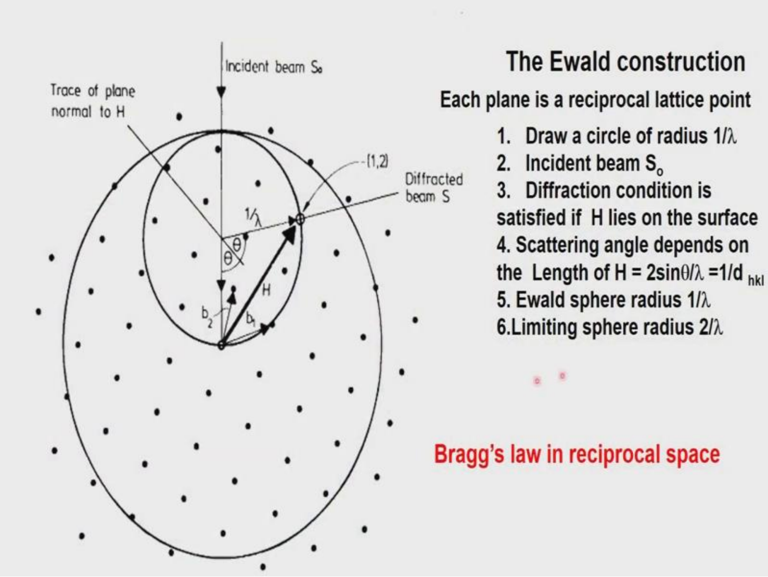

The Ewald construction

Each plane is a reciprocal lattice point

1. Draw a circle of radius $1/\lambda$
2. Incident beam S_o
3. Diffraction condition is satisfied if H lies on the surface
4. Scattering angle depends on the Length of $H = 2\sin\theta/\lambda = 1/d_{hkl}$
5. Ewald sphere radius $1/\lambda$
6. Limiting sphere radius $2/\lambda$

Bragg's law in reciprocal space

So, we just see here that we can do Braggs law in reciprocal space the way in which the number of reflections appear. So, it is always a wonder in many cases that how the how come when we when we start rotating the crystal we get more and more reflections. And, this particular construction helps us to understand how this really happens and how we can get to the diffraction condition.

The one of the major requirements is that the scattering angle depends on the length of H which is 2sin θ/λ. So, this is a major factor which we should remember. So, as the θ angle changes the length of H will change and since length of H will change whenever it satisfies $1/d_{hkl}$ in this particular unit cell; so, you have a unit cell you have $a\ b\ c\ \alpha\ \beta\ \gamma$ and then you have the d values calculated from $a\ b\ c\ \alpha\ \beta\ \gamma$. So, those d values $1/d_{hkl}$ whenever that is equated you will get a reflection.

So, this now, therefore, is can be actually shown in such a way that as we rotate the crystal different parts of this limiting sphere points they will all come and intersect with the Ewald sphere and whenever the intersection is with the Ewald sphere, whenever the intersection is on the surface of the Ewald sphere you will get to the satisfaction of Braggs law and that is why our diffraction pattern is now looking like this.

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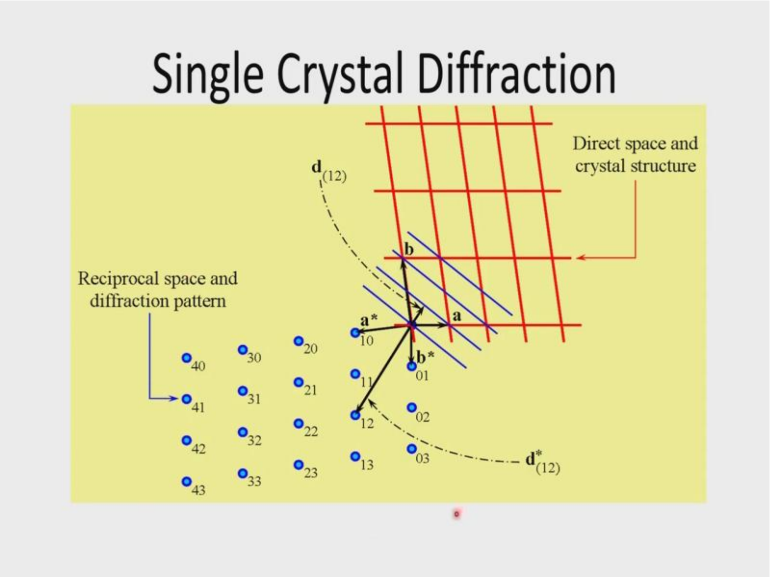

Single Crystal Diffraction

Direct space and crystal structure

Reciprocal space and diffraction pattern

We get a series of spots and these spots therefore, have an identity now. The identity is with respect to the scattering angle and the scattering angle now decides the value of H and H is 2sin θ/λ. So, we can therefore, index these parts in terms of $1/d_{hkl}$ which we of course, can be calling it has d^*_{hkl}. So, we have therefore, d in the real space that is the spacing between planes. Now, it get represented as an identity of a reciprocal lattice point and that reciprocal point will now represent the d*or $1/d_{hkl}$ in the reciprocal space, right.

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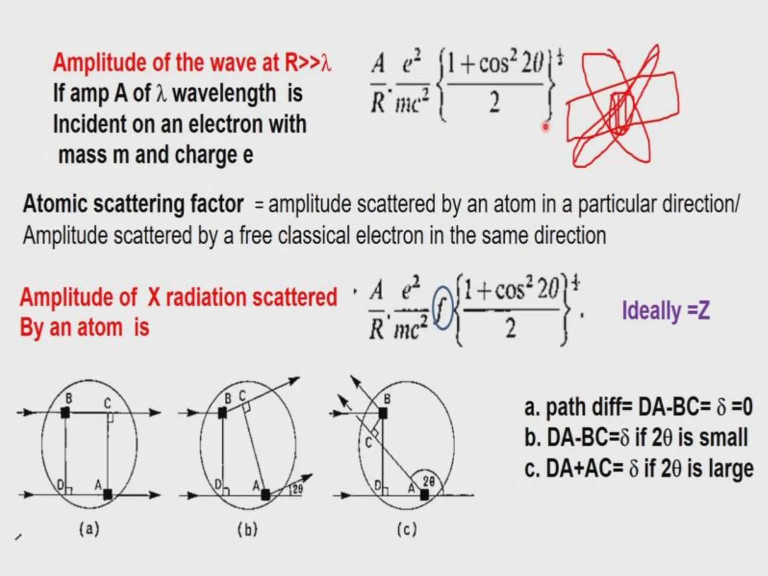

Amplitude of the wave at R>>λ
If amp A of λ wavelength is
Incident on an electron with
mass m and charge e

$$\frac{A}{R}\cdot\frac{e^2}{mc^2}\left\{\frac{1+\cos^2 2\theta}{2}\right\}^{\frac{1}{2}}$$

Atomic scattering factor = amplitude scattered by an atom in a particular direction/
Amplitude scattered by a free classical electron in the same direction

Amplitude of X radiation scattered
By an atom is

$$\frac{A}{R}\cdot\frac{e^2}{mc^2}\,f\left\{\frac{1+\cos^2 2\theta}{2}\right\}^{\frac{1}{2}}.$$

Ideally =Z

a. path diff= DA-BC= δ =0
b. DA-BC=δ if 2θ is small
c. DA+AC= δ if 2θ is large

Now, we have got to an understanding of this we will have now have to see how these spots appear? What is it that is making this spots to appear and why one should be strong one should be weak and so on. Most of us have seen the single crystal diffraction spots or the single crystal diffraction pictures and if you go to diffractometer you will see that being recorded on the CCD camera where you will see them as spots.

Now, this spots can be of different intensities one is strong, another is weak, something else is hardly visible and so on. Even though the geometry is defined, in other words the $1/d_{hkl}$ is defined when once you have $a^*b^*c^*$ their reciprocal lattice vectors when once you have a, b, c you have a^* b^* c^*. So, you have $1/d_{hkl}$ which is the collection of d* values. So, we know where the positions of d* will come depending upon the Braggs law. But, whether the d* value which has come at that particular point has an intensity or not depends upon what is it that is actually causing this diffraction and this now we will I will take you through an exercise where we now understand what is it that is giving us this diffraction.

What is it that is giving us the diffraction it is the interaction between the X-ray beam and the electron density that is associated with that particular position x, y, z in real space. Let me repeat, the position of the atom therefore, the atom now is consisting of electrons as we know. So, it is the electron density which is associated with a point x, y, z which is responsible for the X-rays to do the diffraction. However, the d_{hkl} the $1/d_{hkl}$ in particular that is the positions where the reciprocal lattice points should appear is a geometrical calculation.

So, because it depends only upon the a* b* c* values. So, the geometrically we can identify the positions where the diffraction should occur. However, the intensity of that depends upon how much of electron density that can be associated with that reciprocal lattice point. So, if the reciprocal lattice point is now associated with a large amount of electron density, then you will get the diffraction pattern. Let me draw a little picture to show you what I mean.

Suppose, there is a electron density something like this, this region where there is a lot of electron density and this now lies on a plane which is passing through that like that. So, this could be a one plane, it could be another plane there may be another plane going like that another plane which is going through this and all these planes now contain these electron density.

So, if you now calculate the intensity or if you see now where these spots should come it is already defined by geometry, but the intensity that is associated with the diffraction on; in other words the energy that comes out after scattering depends upon how much of electron density is associated with them. So, these three planes all these three planes will have a large value for the intensity; that means, these will be brighter spots compared to the other weaker spots.

So, if that is the logic that is to be followed we have to find out how this is all happening it is all happening because the amplitude of the wave which comes at very long distances at R, let me go back to the other mode. The amplitude of the wave at distance R which is very far away in terms of the λ value, if the amplitude A of that λ wavelength is incident on the electron with a mass m and a charge e, then the amplitude will be this value which depends upon an expression of this kind. We have to understand what it all means.

So, you have an electron with a charge e and mass m. Now, these this one particular there is no one single electron, there are several electrons in the unit cell, right we associated with a molecule atom position and so on. So, the charge is e and the mass is m the amplitude A that A_0 which we would like to have from the incident radiation is already know us.

So, the incident X radiation has an amplitude A_0. It gets modified after scattering and we observe this amplitude of the wave at a sufficiently large distance R is very much greater than λ. Remember I am using this vector R to identify that we are observing this amplitude corresponding to the vector R which is the scattering vector, which can be replacing in a single crystal by the H which is our scattering vector which is essentially 2sin θ/λ. So, it has to satisfy the Bragg condition.

So, since it satisfies the Bragg condition we get the spot. The amplitude of the spot depends on this quantity and this particular quantity is now A which is the incoming amplitude divided by R. So, if you just send an X-ray beam light intensity for example, light coming from a source in front of us; so, the light will be becoming weaker and weaker as we go to very large distances. In fact, it vary such the square of the distance. So, therefore, when we take it at a very large distance anyway the amplitude gets reduced by that a particular amount proportional to 1 over R. So, amplitude is already reduced.

The fact that it is the electron which is involved in this scattering, we have this e^2/mc^2 factor coming in and then this factor $(1+ \cos^2 2\theta) / 2$ where 2θ is the scattering angle you see this is very crucial this 2θ scattering angle decides where your H vector should come. And therefore, this factor is the one which modifies the amplitude and therefore, you will get different intensities at different positions. So, we therefore, have the amplitude of the value equal to this.

Now, what is it that is causing this amplitude? what is the electron density, right and electron density in our case when we discuss atoms and molecules and collection of molecules in the unit cell depend upon with what atoms these electrons are associated with.

Suppose, we have a structure which as a carbon, nitrogen, oxygen on one hand or a structure with a germanium or even higher elements like zirconium or for that matter even uranium containing compound. So, the electron density associated with these atoms there is a certain size of these atoms which of course, is quantum mechanical calculatable. So, this quantity is also coming from the quantum mechanics evaluation. So, we are not going into the detail of it.

However, it depends upon a factor which is now going to be very very crucial for our calculations and that we call it as the atomic scattering factor. So, if there is a carbon atom, carbon atom will have six electrons. So, at the scattering angle 0, all these six electrons will contribute. So, it is equal to the atomic number. So, if the scattering angle is 0 and the carbon atom is situated there all the electrons will contribute to that one and therefore, it is proportional to 6. I am using the word proportional to 6 because it depends upon where you define your 0 in your crystal system, where is your reciprocal lattice origin. You saw it in the previous diagram it is variable, we can decide where the origin is depending upon where we would like to take the reciprocal lattice point origin and therefore, the atomic scattering factor is proportional to Z the atomic number.

So, depending upon what is the size of that particular atom whether it is carbon or bromine or whatever the number of electrons associated with that particular point will be proportional to Z. But, it so happens that it also with varies with respect to sin θ /λ where in other words it varies with respect to this scattering angle. We already have the amplitude variability shown here for a free electron. Now the amplitude variability is now to be shown for electrons which are associated with the atom. So, we have a position of the atom, we have the core of the atom, we have the surrounding valence electrons and so on, but they are associated now with the atom.

And, therefore, we have to define the atomic scattering factor in a proper way and this is the definition. Amplitude scattered by an atom in a particular direction the two amplitude scattered by a free classical electron in the same direction. So, you consider a free electron and consider the collection of electrons associated with that atom and then the atomic scattering factor is the amplitude that is scattered. So, what happens therefore is, if this is the free electron component we add we multiply it by the factor f which is known as the atomic scattering factor.

So, this is the amplitude of the X radiation scattered by an atom. It is as I said ideally Z because all the electrons should contribute if you just put one atom and send an X-ray beam and this particular atom is now in this in a position like this where this scattering angle is not seen 0 then we will see that the amplitude of the X-ray scattered by the atom is proportional and in fact, more or less equal to Z ideally it Z it will never happen because atoms are all in different positions with respect to some reciprocal lattice origin and therefore, this value you see depends upon this 2θ value.

So, since this depends upon the 2θ value we see that it depends on the scattering angle. So, since it depends on this scattering angle the scattering directions has to be considered very seriously and that is shown in the diagram below. We will try to understand this diagram carefully because this is going to tell us that unfortunately for us this is the limiting step for us. If it were to be individual atoms contributing their entire proportional to Z contribution then there would have been no problem. In fact, that is what happens in the case of a neutron diffraction we will worry about it later.

But, at this particular moment when since X-rays interact with electrons and there is a size of the electron cloud around a given atom and different atoms have different sizes, different contents of electrons and so on. This particular quantity f will also vary with respect to the angle the scattering angle. An illustration of this kinds tells us that if it is not changing the direction if it is coming in and we find electron density at this point A and as electron density at this point B it is not changing any direction going through; that means, there is no change in the path.

The paths simply goes through, but we do find the electron density in its path; that means, if this is atom all the electrons is effectively you know I have considered two small elements of electron density, but there is electron density in the entire sphere which is shown here and all these electron density will now be a part and parcel of scattering and therefore, there is no path difference. So, DA - BC is equal to 0. So, there is no path difference. So, if there is no path difference, there is no phase difference; φ is also 0 and as a consequence the scattering that is coming out from this atom is proportional to the value of Z. In fact, it is equal to Z at ideally 0 value of no change.

But, as we increase or change the scattering direction, we see that as we rotate the crystal different parts of the reciprocal lattice will come and therefore, the angle has to change and that angle changes behaving the Braggs condition. So, as the angle changes if the angles are very small as it shown here in the second diagram which is referred to as b then it is if the angle is small like 2θ indicated here is a small change. So, X-rays are coming here, falling on the these two electron densities and these electron density now decides to diffract the beam. So, it follows the Braggs law and then therefore, this angle 2θ comes into picture and this will be now this scattering vector wave front. So, this yes, the scattered wave will go in this direction.

So, if that is the case then we see that there is a path difference which comes in and this path difference DA - BC will be equal to δ which is the path difference if 2θ is small. So, for smaller 2θ values it goes as DA - BC, but remember that this scattering can be in all possible directions all 360° it can scatter, we do not know, right.

So, when it goes to very high angles what is happening is when you have to take a incoming radiation with a certain intensity and want to deviate that particular incoming radiation by a very large value 2θ as is indicated here; obviously, most of the intensity that is contained in the incoming beam will be absorbed by this atom.

So, as a result the path difference now will become DA + AC. So, the path difference is very very large and for 2θ values large the path difference δ becomes very large and therefore, you get a very interesting behaviour of the variation of f with respective the scattering angle and, the next view graph shows you how it varies.

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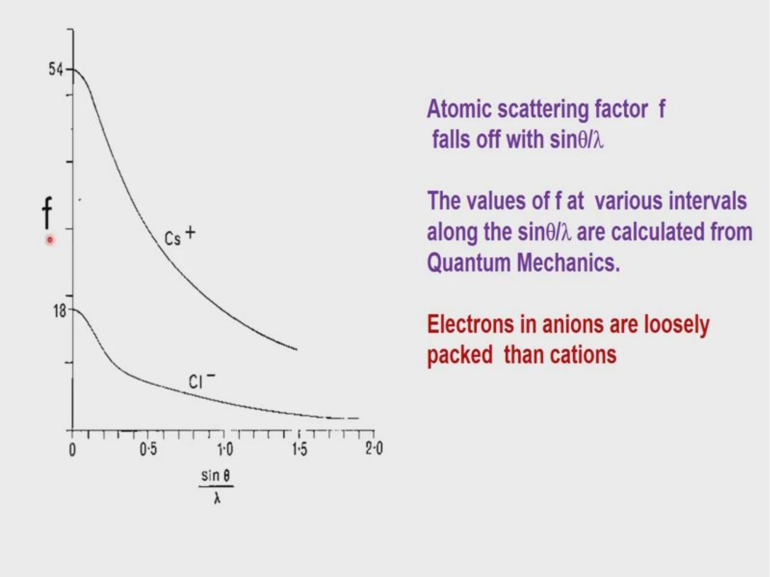

Atomic scattering factor f falls off with sinθ/λ

The values of f at various intervals along the sinθ/λ are calculated from Quantum Mechanics.

Electrons in anions are loosely packed than cations

So, we have therefore, plotting here the scattering atomic scattering factor f and its variability with the sin θ /λ because we would like to say see this independent of the wavelength which we are going to use. So, we show the sin θ values and we show the sin θ /λ so that it is a universally valid curve for all wavelengths which we can use. So, f versus sin θ /λ now varies in this particular fashion.

There are certain things which are associated with this plot which I will discuss as well, but at this moment you see that the atomic scattering factor f falls off with respect to sin θ/λ. So, it is falling off with respect to sin θ /λ and at very large values. It is becoming very very small. So, if you will look at actually a diffraction pattern you will like observe it whether it is a powder diffraction pattern or a single crystal X-ray diffraction pattern.

As you go in the 2θ direction to higher and higher angle the intensity keeps falling very rapidly. In fact, in an organic molecule if you record a powder diffraction pattern you hardly see anything at room temperature, of course; you hardly see anything beyond 35 degree in 2θ that is because these values will go down very fast.

See here the what is plotted is that of Chlorine ion and Caesium ion I have plotted the scattering factors of ions and as a result the Caesium is getting 54 and the Chlorine is getting 18; that means, one extra electron added to Chlorine and one extra electron removed from Caesium and therefore, we get this scattering curve. So, what it also tells is that we can represent a represent also ionized atom positions with respect to the scattering behaviour. So, whether it is in the neutral position or in an ionized position, it depending upon the level of ionization we can actually have the value of f different.

So, for Chlorine the curve will start from 17 at 0 value and then fall off exactly like whatever it is shown here similarly in the case of Caesium. I have taken Caesium and Chlorine specifically because I am we are going to discuss more of Caesium and Chlorine in the coming slides and that is why I have taken Caesium, Chlorine, but it is there for universally for all the elements.

Now, the only problem with hydrogen is that it does not have a core. There is only one electron associated with the hydrogen and therefore, the variation with sin θ /λ with respect that is hard to calculate. In fact, these calculations are done as I have mentioned here the values of f at various intervals along the sin θ /λ are calculated from quantum mechanics. So, we make use of quantum mechanical methodology to calculate the values of every value; that means, we go in interval let us say 0.02 and calculate the values of the how the f value varies with respect to the scattering angle. So, it will fall off with respect to that and comes down fairly rapidly and then more or less stabilizes at higher angles.

This kind of a scattering factor behaviour is there if for all the elements and it so happens that in case of anions in case of anions we have the loosely packed electrons in anions are loosely packed than in the case of cations. So, for example, in the case of Chlorine, you see that the fall off is very very rapid; that means, the starts losing the electrons at lower sin θ /λ angle compare to the Caesium which falls slowly. So, whenever the you have an anion and cation the behaviour of the scattering factor is different from each other. The electrons in anions are loosely packed than cations. So, the fall off with respect to sin θ /λ is dependent upon how tightly the electrons are packed in a given atom.

So, all these values of f versus sin θ /λ at intervals of whatever range we would like to have can be calculated from quantum mechanics and that is not the job of this particular course. So, what we will say is we have taken that value to be already available, so, f varies with respect to sin θ by λ. So, at sufficiently large angles as we see the intensities fall the intensity fall not because the atoms are not there, but the intensity that is associated with the scattering is falling. So, they become poorer and poorer scatter as we go higher and higher in the scattering angle and this is a very serious issue as far as X-ray diffraction is concerned.

So, as I mentioned already hydrogen has no core, so, it cannot be determined generally by a routine X-ray measurement. We have to do some tricks to identify the positions of hydrogen. When we really look at the structure determination protocols we will actually go there and try to see how these analysis can be done.

So, to just to summarize the last two slides now see that the amplitude of the wave is a function which is dependent upon the so called atomic scattering factor. It also depends upon what is the scattering angle. And it so happens that the atomic scattering factor depending upon the angle of the scattering will vary with respect to sin θ /λ and that variation with respect to sin θ /λ has been indicated here. I have taken Caesium and Chlorine I keep this in mind because we are going to use this for a discussion in a few minutes after this discussion.

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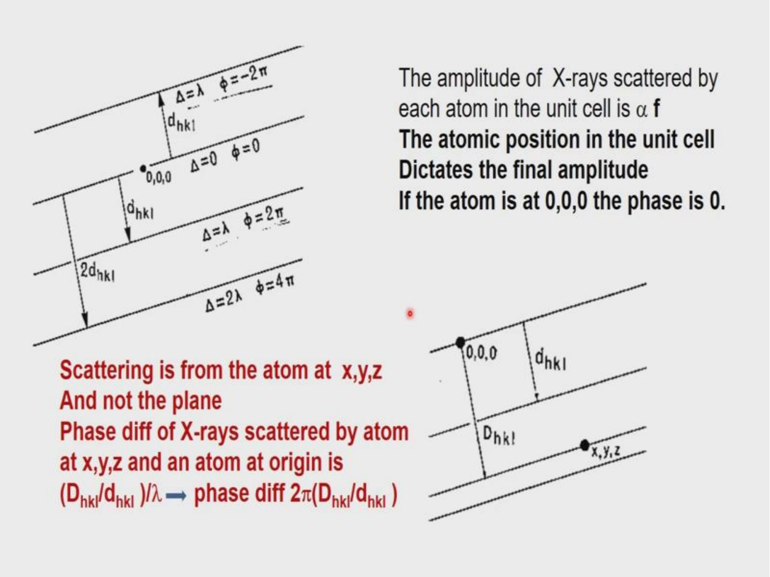

The amplitude of X-rays scattered by each atom in the unit cell is α f

The atomic position in the unit cell Dictates the final amplitude

If the atom is at 0,0,0 the phase is 0.

Scattering is from the atom at x,y,z And not the plane

Phase diff of X-rays scattered by atom at x,y,z and an atom at origin is $(D_{hkl}/d_{hkl})/\lambda \rightarrow$ phase diff $2\pi(D_{hkl}/d_{hkl})$

Now, we go to a situation; you see the thing is we have discussed two issues. This is very important point; the scattering is done by electrons. We have a crystal it is filled with atoms and molecules and so on, the scattering is done by electrons and then we do a diffraction experiment. From what we see from the geometry of the diffraction which we have analysed already in terms of the reciprocal lattice, each and every spot we get is from a plane in the crystal. So, the diffraction is happening, the measurements are with respect to a plane in the crystal.

Whereas, the atoms may or may not lie with respect to a plane, it is not necessary that the atom should be associated with a plane. It is certainly not necessary that the atom should be associated with lattice points. In fact, that is how we have been introduced to the subject in school days that is because it so happens that if we take simple atoms by simple atom I mean let us say copper or you know gold or silver or something like that. These atoms are indeed associated with lattice points in their unit cells. So, when you crystallize an atom, the atom crystals of the atom will have lattice points associated with them to be the positions for the atoms as well. So, that means, that the phase associated with that diffraction which comes with the atom position is zero.

So, you it so happens that the belief that lattice point should have atoms has continued in our mind. So, we have to give a way that belief. What we measure in a diffraction experiment is a measurement which comes as a consequence of Bragg's diffraction which is occurring from a plane in the crystal and we know how to identify planes, we know how to identify those as a reciprocal lattice points, we know the geometry. The geometry is done by the Laue conditions and also by the Braggs equation. So, it is not a continuous distribution it is certain set of regions where these the angle, the scattering angle corresponds to the length of the reciprocal lattice vector whenever that happens we get the diffraction.

So, we have these diffraction points those are coming from planes. The diffraction is coming from the planes in the crystal and therefore, the it is single spots bright and dark and so on. We now just analyse why some are bright and some are dark depending upon the amount of electron density that is present associated with the atom. Now, the atom goes and sits in the unit cell in some position $x_1, y_1, z_1; x_2, y_2, z_2$ and so on.

Now, this x y z is not necessarily to be associated with a lattice point or for that matter any point that can occur inside the unit cell is a possibility of an atom to sit there with. The only thing which is also have to be obeyed is the fact that it has to obey this symmetry rules we have made; that means, if we sitting in a monoclinic system it has to have a minimum twofold symmetry with which it generates the other atoms. So, if there is an atom at x y z with a twofold symmetry, P 2 space group you know that x y z should generate ; that part we know. So, that means, there are two of those atoms inside the unit cell at x y z and y .

So, these both these atoms now will contribute. Now, both these atoms will contribute to every reflection which is satisfying the requirement that the scattering angle should be equal to the length of the reciprocal lattice vector. So, if that is the logic then how do we get the atom positions. So, this is an issue which we will address here after because what we are measuring from the diffraction experiment is the reciprocal lattice geometry by means of which we identify the individual hkl values, the so called reciprocal lattice vectors *hkl* and we also measure the intensity that is associated with a given *hkl*.

So, when you a crystal in a X-ray beam, there X-ray beam passes through the crystal diffraction occurs and you will get various parts and these parts now can be identified with a certain *hkl*. We also can measure the intensity that is associated with it experimentally, at that intensity is the one which is associated with that lattice plane. Now, the requirement that atom should be there or not is not there in this entire experiment. The atoms can be at some point in space which is defined as $x\ y\ z$ or $x_1\ y_1\ z_1$, $x_2\ y_2\ z_2$ depending on the number of atoms and therefore, this issue has to be completely understood and how a position *x y z* contributes to a *hkl* reflection has to be valid and we are now planning to look at that particular phenomena in more detail.

In order to do that we need to see the way in which the planes are oriented in a crystal. We are quite familiar with this now. We can draw a diagram of this kind or we can draw a diagram with respective reciprocal lattice points, but I think in direct space we have still a very clear picture because it is always better to have direct space geometry and therefore, we are drawing this particular diagram.

Now, this diagram tells you that there is a plane which passes through the origin 0, 0, 0. Now, in the previous class we learnt that any point along this particular direction will scatter exactly the same way. So, suppose there is an atom sitting at 0, 0, 0 and then I will put an atom at this position which is moved along this direction with plane within the plane. So, the plane now you remember, plane is a 2-dimensional plane which is coming out towards us. So, any of these points lying with respect to the origin 0, 0, 0 they will all scatter in phase.

So, suppose there are ten atoms in this particular plane, all the ten atoms with scatter in phase φ as the scattering angle the phase associated with this will be 0 and because there is no difference in the path. The path length is 0, path difference as we saw in the previous slide and therefore, we have $\Delta = 0$ and $\varphi = 0$. So 0, 0, 0 if there is an atom here it will now contribute its entire scattering power to this particular plane. So, this plane could be some *hkl* associated with 0, 0, 0 and this the first plane away from the origin.

Now, we should consider the first plane away from the origin it has to satisfy the Bragg condition and what is the Bragg condition $2d \sin \theta = \lambda$. So, the path difference should be λ. So, the from the origin every diffraction plane which will come will be a path difference or multiple of path difference associated with d_{hkl} we have seen that it depends upon the value of $n\lambda$, n could be 1, 2, 3, 4, 5, 6 to whatever.

So, if we consider n is equal to 1, then the path difference is Δ equals λ and a corresponding phase change will be 2π. How is that coming? The Δ path difference is Δ is the path difference, the phase difference is 2φ you go back to the discussion where we had the how the path length and a phase they come with respect to each other R going to

R+ΔR and that gave a path difference and that Δ R now gets multiplied by a factor of 2π in order to get the phase difference which is a reduction in the phase. So, addition of a longer path length will reduce the corresponding phase and therefore, we get a phase difference which is 2π.

So, if delta is λ/2 then we get value a φ value of π. Now, how does that happen? It does cannot happen here, but suppose it can happen then we will have to remember that Δ can be then λ/2. Keep that in mind we will solve that mystery in a few minutes. So, if Δ is λ/2, then φ will be equal to π remember that and so on. I mean if Δ is λ/3, λ/4 etc.

Now, under what circumstances we will have that kind of a phase contribution to the given crystal because at this moment we do not have any such contribution. By definition the first plane out of the origin plane; plane passing through the origin must have a path difference of λ by Braggs law and therefore, since Braggs law says it is the only way in which we can have this particular plane which is now at a distance of d_{hkl} will give us the diffraction.

The next path which we will next plane we will get will be the $2d_{hkl}$ there the Δ is 2 λ, φ is 4π. So, these numbers have to be now integers. We can of course, go in the negative direction as well we can go up from the 0, 0, 0 plane and we get a phase difference, which is minus 2π again the value of Δ is λ it is moved by d_{hkl}, but since it is in the opposite direction the phase change will be minus 2π. Now, what is 2π? 2π is 2 times the π value. What is π? What is 2π? 2π is 360 degrees is it or 180 degrees, which is correct? Think about it.

We will leave at leave you at this particular point and then one once you tell me what is 2π we will go further or once you realise what is 2π we will go further.