Chemical Crystallography
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Lecture - 32
Derivation of Friedel's Law from Structure Factor by Vector Space Diagram

Welcome back to this course of X ray crystallography. In the previous couple of lectures, we have learnt about the Structure Factor and scattering factor. So, we would like to continue in this direction one; in next few lectures and we will try to understand the importance of structure factor, and how one can relate structure factor to electron density through a Fourier transformation, and then also we will try to understand the origin of systematic options using these structural factor equations.

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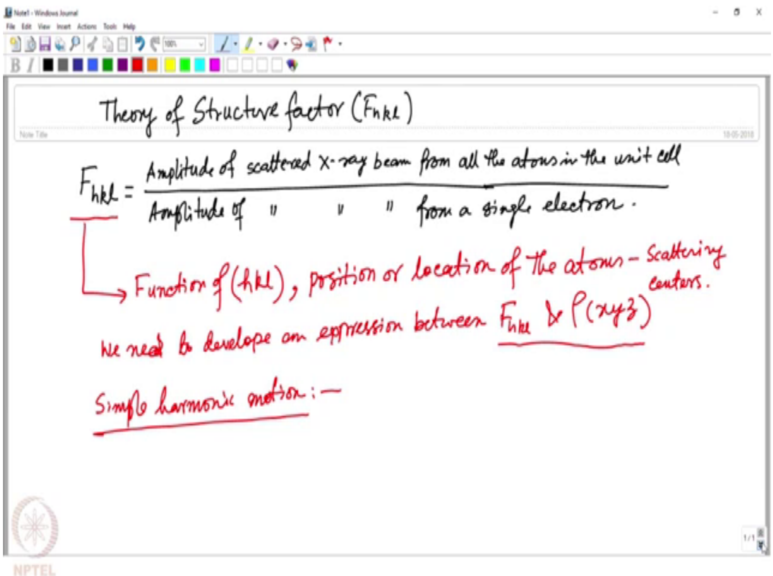

So, the theory of structure factor as we are continuing theory of structure factors; which we write as F h k l and as we have already understood that F h k l is nothing but the ratio of the amplitude of scattered x ray beam from all the atoms in the unit cell divided by the amplitude of scattered x ray beam from a single electron. So, this atomic scattering factor, sorry. So, this structure factor capital F h k l it is a function of h k l; that means, for different plane h k l if the value of this F h l will be different; because the plane that we are talking about have different orientations.

So, different atoms present in the unit cell will have different contribution to the diffraction factor that is the F h k l on that particular plane. So, the scattered structure factor for this plane will be different from that plane and it will be different from this plane will be different from that plane all possible planes will have different scattering factors. So, it is a function of that h k l that is the miller indices of the planes and position or location of the atoms. Because these atoms are actually the scattering centres which are scattering centres.

So, what we need is that we need to develop to develop an expression between F h k l and rho x y z; where rho x y z is the electron density associated with the atom location x y z. And there may be n number of atoms located at n different sites in the unit cell. So, we need a nice equation to equate these 2 quantities F h k l and rho x y z. So, to understand this what one needs to do is to go through a process where we assume we are having a simple harmonic motion. And from there we would extend our understanding.

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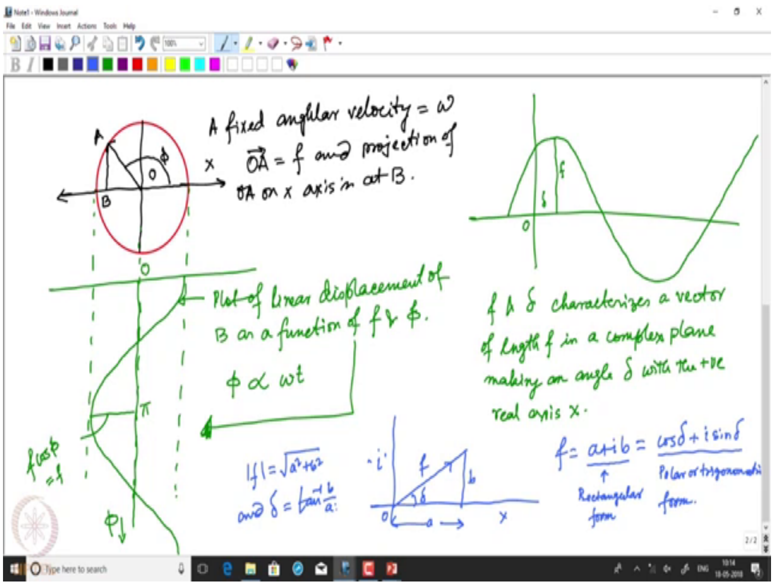

Suppose we have a point A moving in a circular path. So, that point A moves in a circular path with a cantered at O. And this point A has a fixed angular velocity equal to omega. So, at any given point of time, the projection of O A on say this is the x axis is O B and O A represents the vector f, and projection of O A on x axis is at B. So, at a given position of A making an angle phi with the x axis. And this being rotated along the circumference of the circle at a given fixed angular velocity omega, this represents a simple harmonic motion.

So, if I try to plot the linear displacement of B with respect to the origin O, this motion would look like a curve like this. So, this is the plot of linear displacement of B as a function of f and phi. So, at this direction is your direction of phi and we started here at 0, this is the direction of phi, and the maximise is reached when phi equal to pi and that is equal to f cos phi equal to f at phi equal to pi. If the angular velocity omega is constant, and then phi is proportional to omega t. So, this will represent the linear displacement of B along the direction of phi. So now, suppose if there is a phase difference, we draw the same curve with a phase difference of delta with respect to the origin. So, in that case, these terms f and delta also characterizes a vector of length f in a complex plane making an angle delta with the positive real axis x.

So, the situation is like this. So, in that this is the drawing of f in a complex plane where f makes an angle delta with the x axis. So, one can write f equal to a plus ib, which is nothing, but cos delta plus i sin delta. So, this x ray representation a plus ib is termed as the rectangular form. And cos delta plus i sin delta is store termed as the polar odd trigonometric form.

So, from here one can write the value of mod f equal to; this is small f, value of function f equal to a square plus b square, and delta equal to tan inverse b by a. This is how one can represent a simple harmonic motion f of particle in a circular path with a vector f.

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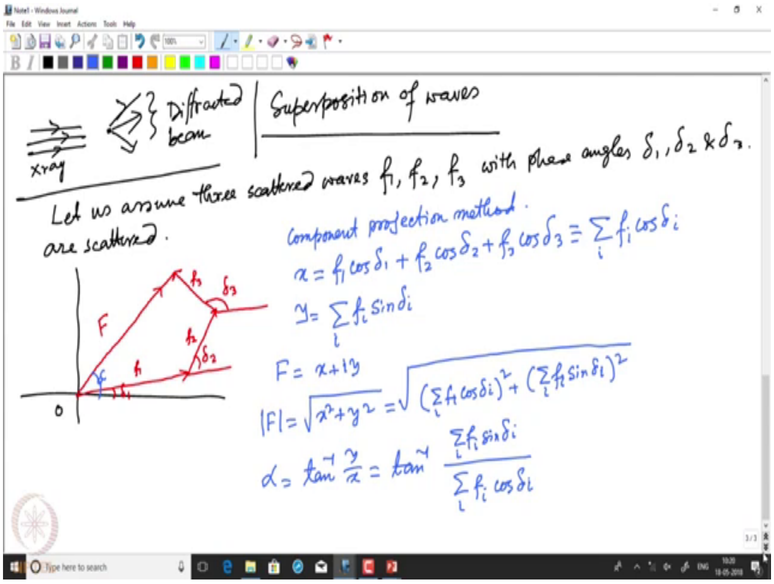

Suppose, we have a crystal here and x ray beam is impinging of the crystal, and it detracts in all possible directions.

So, when such things happen, multiple waves are scattered at various directions. So, then we need to understand how these waves are superposing. So, we need to little bit of superposition of waves. So, let us assume 3 scattered waves f 1, f 2 and f 3 with phase angles delta 1, delta 2 and delta 3 are scattered; they are scattered simultaneously.

So, in a vector space diagram we can represent these 3 waves in this way. Suppose, this is f 1, this is f 2 and f 3 is in a different direction like this. So, the overall wave the summation is capital F. This f 1 is making delta 1 here, f 2 is making delta 2 death and f 3 is making a phase angle of delta 3 here.

So now, if we use the component projection method to do this addition, then the corresponding x component turns out to be f 1 cos delta 1 plus f 2 cos delta 2 plus f 3 cos delta 3 which can be written using a summation over i f i cos delta i. Similarly, y can be represented as some over i if i sin delta i. Whereas, F equal to x plus i y. So, modulus of F is nothing but square root of x square plus y square which is now equal to sum over i f i cos delta i square plus sum over i if i sin delta i whole square and then a square root of this.

And the overall angle of f that is the phase angle of f which is alpha, can be written as tan inverse y by x which is equal to tan inverse some over i f i sin delta i by some over i f i sin, sorry cos delta i. So, this is how the superposition of waves can be calculated and we learnt the same in the previous class as well.

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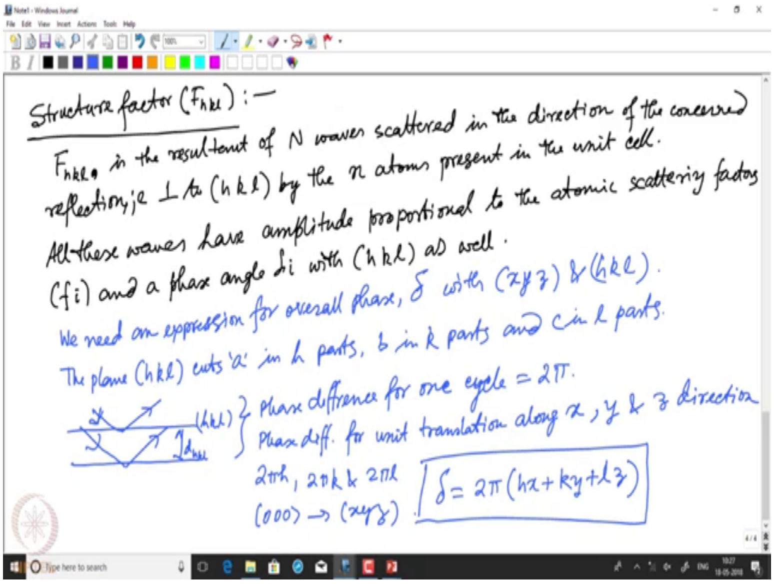

So, what does a structure factor represent? F h k l the structure factor is the resultant of n waves scattered in the direction of the concerned reflection; that is, perpendicular to the plane h k l by the n as small n atoms present in the unit cell. All these waves have an amplitude proportional to the atomic scattering factors which is represented as f i and a phase angle delta i with h k l as well. So, what we need? We need an expression for the overall phase delta with x y z and h k and l.

So, what we know is that the plane h k l cuts a in each parts, b in k parts and c in l parts. So, when we have a set of h k l planes with a distance d h k l and a set of reflections at a set of wavelengths x ray wavelength, sorry, when a diffraction occurs from these 2 planes h k of in this h k l, the phase difference for one cycle is equal to 2 pi. So, the phase difference for unit translation along x y and z direction would be equal to 2 pi h 2 pi k and 2 pi l for corresponding be phase difference about one cycle.

So, the phase difference between 2 points 0, 0, 0 and x, y, z is nothing but delta which is equal to 2 pi h x plus k y plus l z. This is the expression of phase difference between the sets of reflections from a set of parallel planes with indices h k and l.

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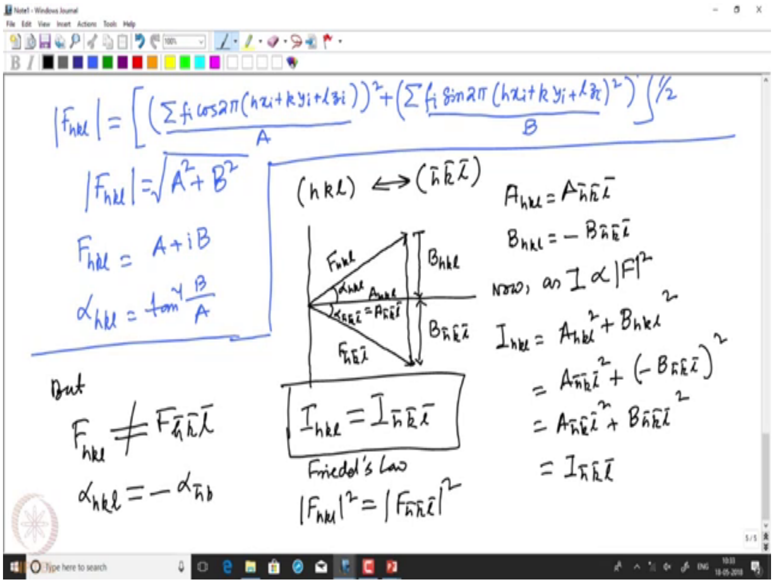

So, one can calculate the mod of F h k l as sum over f i cos 2 pi h x i plus k y i plus l z i whole square, plus sum over f i sine 2 pi h x i plus k y i plus l z i square over all square root.

So, we write this term as A and B sine term as B. So, one can write F h k l is equal to A square plus B square, square root of that. So, one can write F h k l equal to A plus i B and alpha h k l is equal to tan inverse B by A. So now, let us see a situation for 2 different values of h k l which are related by a centre of inversion; that means, I am talking about h k l and h bar k bar l bar.

Let us first see pictorially. Suppose, this vector represents f h k l and this vector represents F h bar k bar l bar. If we join the 2 tips, this portion represents B h k l and this portion represents B h bar k bar l bar and here it is A h k l equal to A h bar k bar l bar. The phase angle for the h k and reflection is alpha h k l, phase angle for the f h bar k bar l bar is alpha h bar k bar l bar.

So now, from the figure we can easily see that a h k l is equal to A h bar k bar l bar, B h k l is equal to minus of B h bar k bar l bar is of opposite sign. And now as I is proportional to F's mod of F square we can write I h k l equal to A h k l square plus B h k l square which is equal to A h k h bar k bar l bar square. Because A h k l equal to A h bar k bar l bar, and B h k l equal to minus of B h bar k bar l bar square. Which is equal to A h bar k bar l bar square plus B h bar k bar l bar square; which is equivalent to I h bar k bar l bar.

So, that means, we arrived at a situation where I h k l is actually equal to I h bar k bar l bar. What is this expression called? We have already discussed about this. This expression this relationship is called the Friedel's law. See although, this I h k l is equal to I h bar k bar l bar, which actually means mod of F h k l square is equal to mod of F h bar k bar l bar square, but not f h k l equal to f h bar k bar l bar. So, what we should actually write is, but h bar f h k l is not equal to f h bar k bar l bar, because they have the angle different; which means the alpha h k l is equal to minus of alpha h bar k bar l bar.

So, today we have seen in this lecture, how one can derive the expression for structure factor once again using vector space diagram and involving the complex numbers. And from there how to show that the Friedel's law can we arrived at using these structure factor expressions. So, we will continue in the next class with the structure factor having Andril relationship with electron density.