Chemical Crystallography
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Lecture - 31
Experimental Methods and Theoretical Understanding of X-Ray Diffraction

Welcome back to the course of Crystallography. In the previous lecture we were talking about the atomic scattering factor f which we defined as the ratio of the amplitude of scattered radiation by an atom divided by the amplitude of scattered x ray by a single electron.

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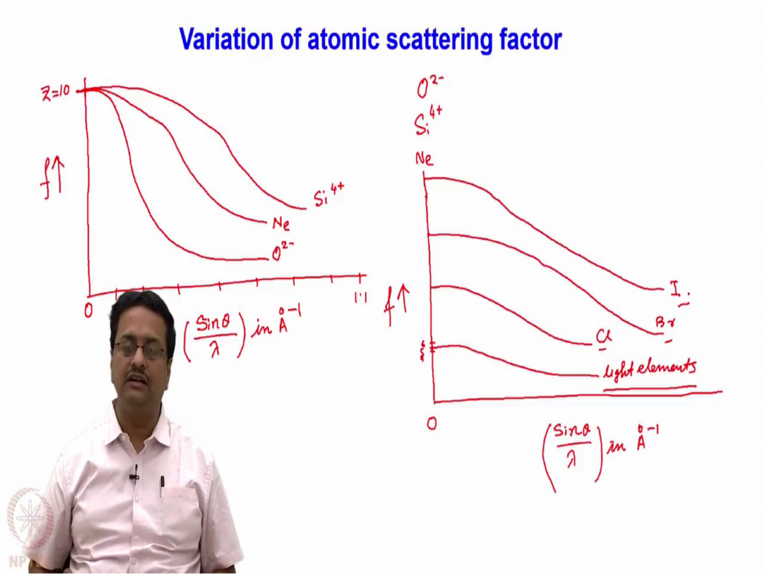

Variation of atomic scattering factor

And then we understood the variation of atomic scattering factor with sin theta by lambda for different nuclei, and we indicated that the scattering factor or scattering power of an element reduces drastically with the increase in the scattering angle theta. So, with sin theta by lambda the scattering power of every element reduces very significantly as a result at a higher angle. We do not get a very strong diffraction from many most of the crystals.

And also we indicated that for light elements as we have shown here, the scattering power is very less and heavier the element we have stronger and stronger diffraction capability from those elements.

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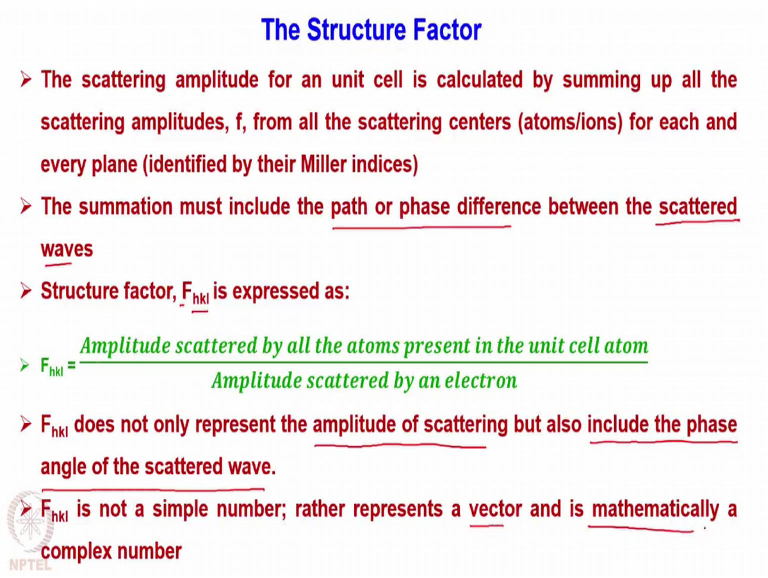

The Structure Factor

- The scattering amplitude for an unit cell is calculated by summing up all the scattering amplitudes, f, from all the scattering centers (atoms/ions) for each and every plane (identified by their Miller indices)
- The summation must include the path or phase difference between the scattered waves
- Structure factor, F_{hkl} is expressed as:
- $F_{hkl} = \dfrac{\textit{Amplitude scattered by all the atoms present in the unit cell atom}}{\textit{Amplitude scattered by an electron}}$
- F_{hkl} does not only represent the amplitude of scattering but also include the phase angle of the scattered wave.
- F_{hkl} is not a simple number; rather represents a vector and is mathematically a complex number

So now we will try to see what do we mean by structure factor a new (Refer Time: 01:41) see when we have a set of scattering centres set of atoms within the unit cell following a particular symmetry, then the scattering from each one of those atoms located at different sites that is different values of x i y i z i, how that those elements are scattering, and how one can sum up those scattering amplitudes to understand the intensity that is coming up from one particular lattice plane.

So, what we are trying to do is, the scattering amplitude of an unit cell is calculated by summing up of all the scattering amplitudes, that is the f, from all these scattering centres which are atoms or ions for each and every plane that one can consider in the crystal. The summation must include the path difference between the scattered waves.

The summation must include the path or phase difference between the scattered waves. So, the structure factor which is represented by the uppercase letter f with suffix h, k, l is mathematically expressed as the ratio of amplitude scattered by all the atoms present in the unit cell by amplitude scattered by an electron.

If h, k, l does not only represent the amplitude of scattering, but also includes the phase angle of this scattered wave. This phase angle is important; we will come to this discussion at a later stage. Today if h, k, l the structure factor is just not a simple number. It represents a vector and in mathematical terms it represents a complex number.

So, let us see what do we understand by the structure factor.

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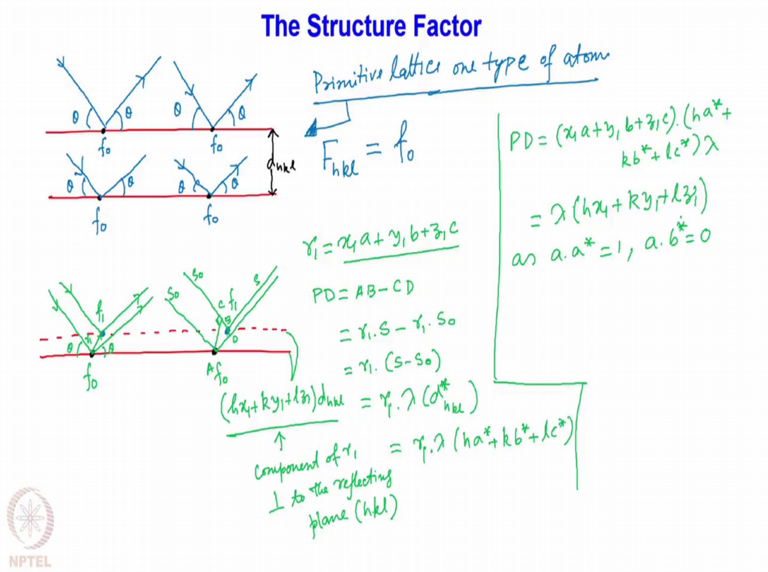

The Structure Factor

Primitive lattice one type of atom

$F_{hkl} = f_0$

$r_1 = x_1 a + y_1 b + z_1 c$

$PD = AB - CD$

$= r_1 . S - r_1 . S_0$

$= r_1 . (S - S_0)$

$(hx_1 + ky_1 + lz_1) d_{hkl} = r_1 . \lambda (d^*_{hkl})$

$= r_1 . \lambda (ha^* + kb^* + lc^*)$

Component of r_1 $\perp$ to the reflecting plane (hkl)

$PD = (x_1 a + y_1 b + z_1 c) . (ha^* + kb^* + lc^*) \lambda$

$= \lambda (hx_1 + ky_1 + lz_1)$

as $a.a^* = 1$, $a.b^* = 0$

Suppose we have 2 scattering centres on 2 parallel planes, I designate them in black, and the distance between the these 2 parallel planes is nothing but d h, k, l. Here if we now consider the x ray diffraction that is we have incident beam falling on this point and getting scattered. This is the incident beam that is the diffracted beam. It is going in the direction theta, and the same for the other atom scattering at a different location, which is again theta and theta and the atomic scattering factor for those atoms are same because they are identical atoms.

So, the same can happen for the plane which is just below this with the same angle of incidence and diffraction, and these atoms are all same having atomic scattering factor f 0. So, if we consider a primitive lattice of one type of atoms, then the situation which I have drawn is justified. So, then when we have only one type of atom, the corresponding structure factor F h, k, l is nothing but the atomic scattering factor f 0. Because all the atoms are located at (Refer Time: 06:57) in case of primitive lattice, you have 8 atoms located at 8 corners of the unit cell and all of them being the same, the summation is nothing but it is the atomic scattering factor of f 0.

So now if we have 2 different scatterers which now I am going to drop below. Suppose, you have one set of scatterers on this plane and the other set of scatterers present in a plane just above it, then if you consider the atom positions like before; where we have one atom here, the same kind is present at a distance here. And a different atom the second type of atom is located at this point and this point with respect to the first.

So, then when the diffraction is considered, the incident beam gets diffracted like this, and simultaneously the incident beam, gets diffracted like this for the second type of atom as well. So now, if this angle is theta, this is also theta and now we try to drop perpendicular from the atom point here. And we drop a perpendicular from there, and the paths A C and B D are to be considered.

So, we have the unit vector like before s 0 and s going like that. So now, we can think of that, the scatterer here is scattering factor f 0, scatterer there is f 1. And the unit vector from f 0 to f 1 is nothing but r 1. So, the position vector r 1 is equal to x 1 a plus y 1 b plus z 1 c.

So now if we try to calculate the path difference between the 2 scattered waves from the atom located at a with scattering factor f 0, and atom located at b with scattering factor f 1. The path difference the path difference is A B minus C D, and which means A B equal to r 1 s minus r 1 dot s minus r 1 dot s 0, which means it is equal to r 1 dot s minus s 0. As before s and s 0 are unit vectors in the direction of in diffracted beam and the incident beam.

So now the difference here is nothing but h x 1 plus k y 1 plus l z 1 which is equal to, sorry, multiplied by d h, k, l which is equal to the component of r 1 perpendicular to the reflecting plane, that is the plane h, k, l.

So now as we know this s minus s 0 can be written as lambda d square d star h, k, l. So, we can write r 1 lambda d star h, k, l which is equal to r 1 dot lambda h a star plus k b star plus l c star. So now, one can rewrite the path difference, we can rewrite the path difference as we replace r 1 by x 1 a y 1 b z 1 c, and take a dot product with h a star plus, k b star plus l c star into lambda,; which is equal to lambda h x 1 plus k y 1 plus l z 1. As a dot a star is 1, and a dot b star is equal to 0.

So, the path difference is now integral multiple of lambda times the component of the r 1 along the perpendicular direction of h, k, l plane. So now, considering a vector phase diagram; where the length of the vectors are proportional to the atomic scattering factors so, we consider a vector phase.

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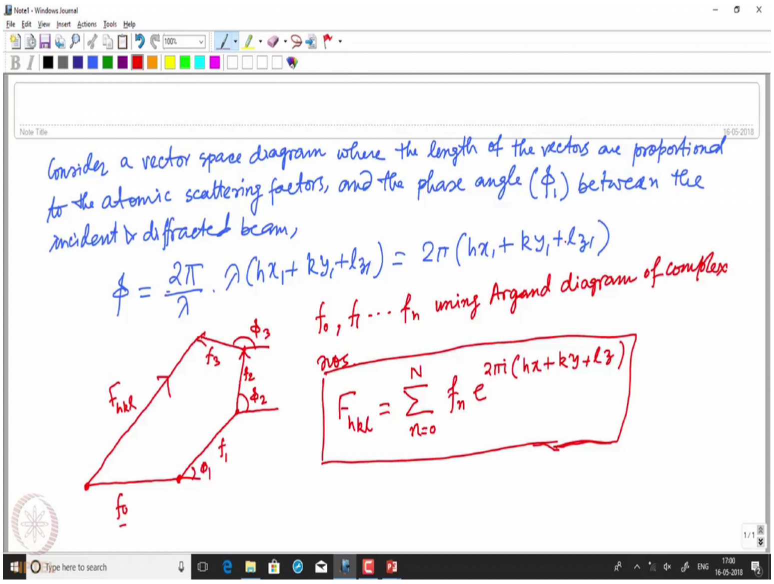

Consider a vector space diagram where the length of the vectors are proportional to the atomic scattering factors, and the phase angle (ϕ_1) between the incident & diffracted beam,

$$\phi = \frac{2\pi}{\lambda} \cdot \lambda (hx_1 + ky_1 + lz_1) = 2\pi (hx_1 + ky_1 + lz_1)$$

$f_0, f_1 \cdots f_n$ using Argand diagram of complex nos.

$$\boxed{F_{hkl} = \sum_{n=0}^{N} f_n e^{2\pi i (hx + ky + lz)}}$$

We consider a vector space diagram; where the length of the vectors are proportional to the atomic scattering factors.

And the phase difference or phase angle rather the rotate phase angle phi 1 between the incident and diffracted beam. We can write the phase angle phi is equal to 2 pi by lambda into the component which is lambda h x 1 plus k y 1 plus l z 1; which is nothing but 2 pi h x 1 plus k y 1 plus l z 1.

So, this is the case with 2 scatterers, 2 atomic scatterers present in the lattice. So now, if we consider that we have a multiple scatterers, then what can we draw? We can draw the following figure. Suppose for a scatterer located here, the atomic scattering is in this direction and we write it as f 0. From the next scatterer located here it makes a phase angle of phi 1 and we cut it here, the next atom scatters in this direction as f 2 making an angle phi 2. And the next scatterer is scattering in this direction f 3 with an angle phi 3.

So, the overall scattering from the origin is the sum of all these scatterings which we write as F h, k, l the structure factor. So, here we are summing up all scatterings f 1, f 2, f 3 and so on in slowly changing scattering angle phi. Then we need to do a sum up of all these scatterings to get the value for the scattering factor F h, k, l. So, this sum up is not simple summing up of numbers. Instead of adding these vectors, graphically, we added using the argon diagram of complex numbers. So, we add these scatterings f 0, f 1 up to f n using argon diagram of complex numbers.

So, this sum can be written as F h, k, l is equal to sum over n equal to 0 to n f n e to the power 2 pi i h x plus k y plus l z. This is the expression for the structural factor present structure factor computed for a multi atomic system in a crystal structure. Let us see how one can calculate the structure factor for multi electronic systems.

So, let us take the example of caesium chloride.

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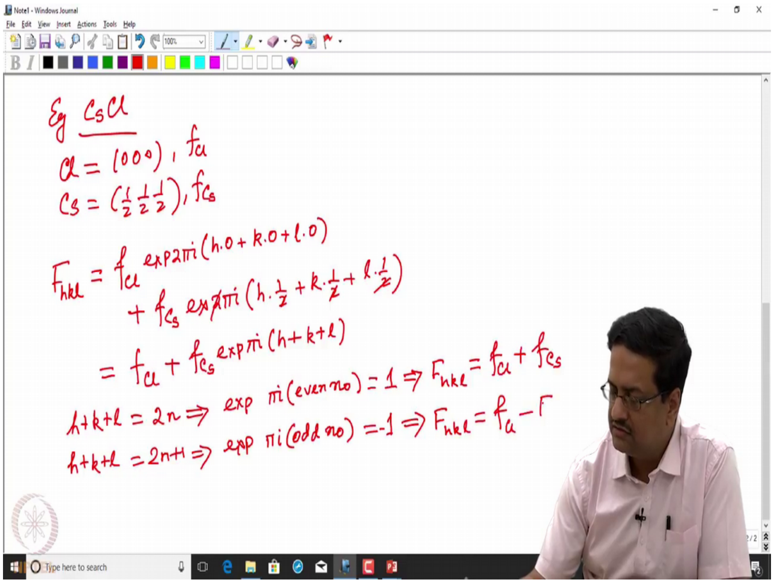

Eg $\underline{CsCl}$

$Cl = (000), f_{Cl}$

$Cs = (\frac{1}{2}\frac{1}{2}\frac{1}{2}), f_{Cs}$

$$F_{hkl} = f_{Cl} \exp 2\pi i(h.0+k.0+l.0) + f_{Cs} \exp \cancel{2}\pi i(h.\tfrac{1}{2}+k.\tfrac{1}{2}+l.\tfrac{1}{\cancel{2}})$$

$$= f_{Cl} + f_{Cs} \exp \pi i(h+k+l)$$

$h+k+l = 2n \Rightarrow \exp \pi i(\text{even no}) = 1 \Rightarrow F_{hkl} = f_{Cl} + f_{Cs}$

$h+k+l = 2n+1 \Rightarrow \exp \pi i(\text{odd no}) = -1 \Rightarrow F_{hkl} = f_{Cl} - F$

In this case, as we have already discussed the fluoride ions are located at 0, 0, 0 and caesium ions are located at half, half, half, we write the corresponding atomic scattering factors as f c l and f c s. So, if we try to calculate the scattering factor F h, k, l for this simple cubic structure, we write the sum as f c l exponential 2 pi i h x k y plus l z. Remember this x y and z are zeros here plus f c s exponential 2 pi i h into half k into half plus l into half. That is the atomic coordinates of caesium. So now, the exponential term at the beginning the in the first term is e to the power 0 is 1. So, it is nothing but f c l plus f c s e to the power or exponential. 2 gets cancelled in inside and outside. So, it is pi i h plus k plus l.

So now for different values of h, k and l if we have h plus k plus l equal to even number; that means, e to the power 2 pi i even number is equal to 1, which then indicates that structure factor F h, k, l is nothing but f c l plus f c s. If this sum h plus k plus l is odd so, in that case exponential 2 pi, sorry, exponential pi i exponential pi i odd number is equal to minus 1 which indicates the structure factor comes down to h, k, l, F h, k, l is equal to f c l minus f c s.

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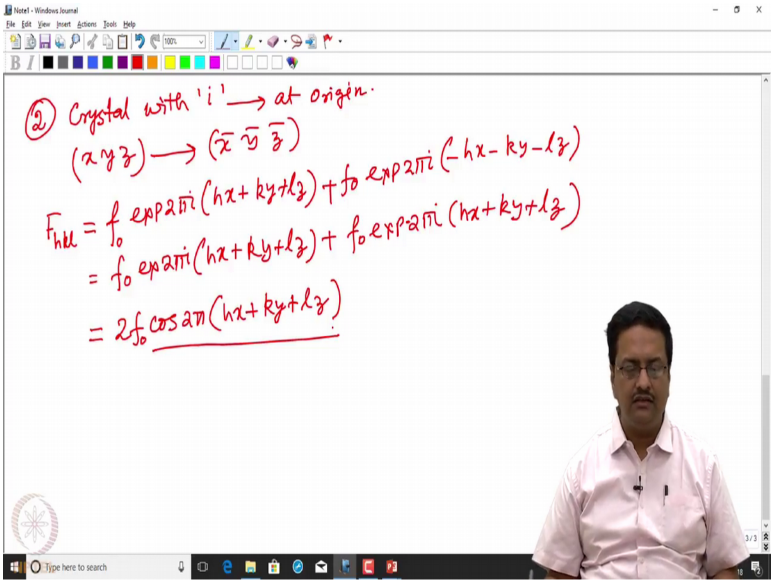

② Crystal with 'i' ⟶ at origin.

$(x\,y\,z) \longrightarrow (\bar{x}\,\bar{y}\,\bar{z})$

$$F_{hkl} = f_0 \exp 2\pi i(hx+ky+lz) + f_0 \exp 2\pi i(-hx-ky-lz)$$

$$= f_0 \exp 2\pi i(hx+ky+lz) + f_0 \exp -2\pi i(hx+ky+lz)$$

$$= 2f_0 \underline{\cos 2\pi(hx+ky+lz)}$$

Now, let us consider the situation where a crystal has a centre of inversion. So, we consider a crystal with I. And we assume that this I is at the origin. So, if we have atoms at x, y and z; then we should have another atom at x bar y bar and z bar. So now, if we try to calculate the value of F h, k, l what do we get we have f remember the 2 atoms at x y z n and x bar y bar z bar are same.

So, we write the atomic scattering factor as f 0 for both of them exponential 2 pi i h x, plus k y plus l z plus f 0 exponential 2 pi i minus h x minus k y minus n z; which means it is equal to f 0 exponential 2 pi h x plus k y plus l z, plus f 0 exponential 2 pi i with a minus sign h x plus k y plus l z.

On expanding these 2 terms in terms of cos and sin and simplifying one can get 2 f 0 cos 2 pi h x plus k y plus and z. So, in case of central symmetric structure, the sin terms have disappeared. So, for the central symmetric structure what we see is that the structure factor F h, k, l is only represented by a cos term. So, in this lecture we have discussed about the scattering factors, they are talked about the structure factors, how these structure factors can be calculated for different systems.

And I have covered these 2 lectures the previous one and this one from the textbook of Hammond the x ray crystallography book by Hammond. In chapter 8 and 9 so, I would like you to go through these 2 chapters, then it will be clearer to you. So, in the next class we will continue to a work with the structure factor expressions, and we will learn how to derive the systematic absence conditions from structure factors.