# Chemical Crystallography
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## Lecture- 30
## Laue's and Bragg's Analysis

Welcome back to this course of crystallography. In the previous lecture, we have learnt about the experimental aspects of single crystal X ray diffraction, data collection how to carry out the experiment and what are the parameters that one needs to worry about. So, in today's lecture, we have initially first going to learn a few things regarding the X ray diffraction methodologies theories. And we will again go back to Laue's experiment and Laue understands of X ray diffraction and then, how Bragg's understanding improved the method concept of X ray diffraction.

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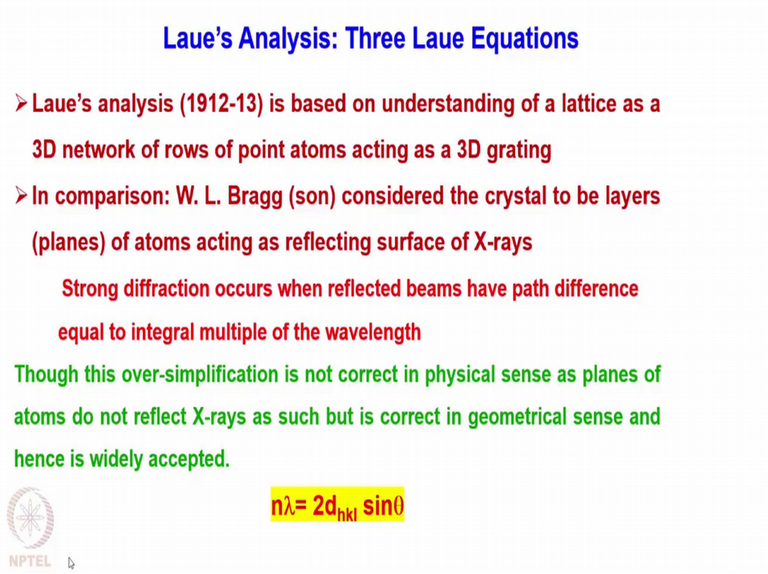

**Laue's Analysis: Three Laue Equations**

- Laue's analysis (1912-13) is based on understanding of a lattice as a 3D network of rows of point atoms acting as a 3D grating
- In comparison: W. L. Bragg (son) considered the crystal to be layers (planes) of atoms acting as reflecting surface of X-rays

  Strong diffraction occurs when reflected beams have path difference equal to integral multiple of the wavelength

Though this over-simplification is not correct in physical sense as planes of atoms do not reflect X-rays as such but is correct in geometrical sense and hence is widely accepted.

$n\lambda = 2d_{hkl}\sin\theta$

In about 1920 1930, the Laue's analysis was based on the understanding of a lattice as a 3 dimensional network of rows of atoms acting as a 3 dimensional grating. So, he considered that each one of these atoms arranged in a specific row along x y and z each of them diffract X rays in the same way and he derived a few equations explaining those X ray diffraction coming out of those rows of elements or atoms which he assumed to form a 3 dimensional grating.

In comparison, William Lawrence Bragg, the son Bragg considered the crystal to be layers or planes of atoms acting as reflecting surface of X rays. So, considering those atoms, instead of a row of atom, he considered those rows of atoms formed a particular plane and 2 such parallel planes cause diffraction just like reflection and he derived a very simple equation.

So, in his understanding, strong diffraction occurs when reflected beams have path difference equal to the integral multiple of wavelength. Although, this oversimplification is not fully correct in physical sense as planes of atoms do not actually reflect a trace as such, but it is correct in geometrical sense and hence this understanding is widely accepted.

And, as we all know the mathematical expression for Bragg's law is n lambda equal to 2 d h k l sin theta where lambda is the wavelength of radiation used, d is the distance between the 2 parallel set of planes and theta is the angle of diffraction.

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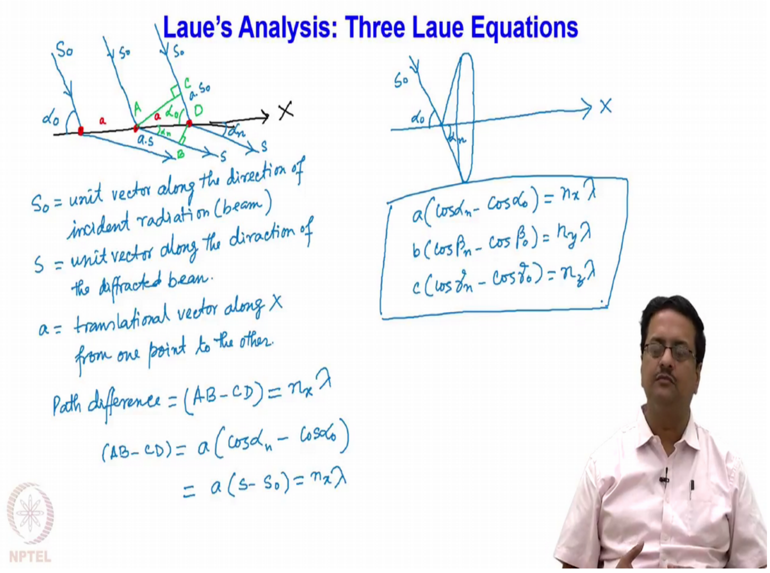

Laue's Analysis: Three Laue Equations

$S_o$ = unit vector along the direction of incident radiation (beam)

$S$ = unit vector along the diraction of the diffracted bean.

$a$ = translational vector along X from one point to the other.

Path difference $= (AB - CD) = n_x \lambda$

$(AB - CD) = a(\cos\alpha_n - \cos\alpha_0)$

$= a(S - S_0) = n_x \lambda$

$$\boxed{\begin{aligned} a(\cos\alpha_n - \cos\alpha_0) &= n_x \lambda \\ b(\cos\beta_n - \cos\beta_0) &= n_y \lambda \\ c(\cos\gamma_n - \cos\gamma_0) &= n_z \lambda \end{aligned}}$$

So now, let us try to understand the concept using Laue's analysis and we would try to arrive at the Laue equations of X ray diffraction. As I said, already in Laue's understanding, the crystal was considered to be a lobe of atoms at equal spacing along x y and z. So, here I am considering one direction only and the distance between the 2 lattice points is nothing but a along the direction of x.

Now, if I assume that the incident radiation is falling on this atom, 2 set 2 reflect 2 incident beams falling on 2 consecutive atoms like this and they make an angle of alpha 0 with x direction and the diffracted beam goes like that.

So, the deflected beam makes an angle alpha n with respect to the direction of X rays, sorry with respect to the x direction. So, what he considered is the incident beam as S 0, where S 0 is the unit vector along the direction of incident radiation or incident beam and S as the unit vector along the direction of the diffracted beam. And as I have already indicate a is the translational vector along x from one point to the other.

So, with the consideration of a row of atoms located at unit vectorial distance a on x axis, along x axis they are being radiated by an X ray of a particular wavelength and that particular X ray is termed as a 0 indicating the it is unit vector along the direction of the beam and S is the unit vector along the direction of the diffracted beam.

So now, if we try to see what is the path difference between the incident beam, and the diffracted beam we would like to draw a perpendicular from this point on to the other incident radiation. So, if this particular point is named as A and this is named as C, this AC is perpendicular to the incident beam.

Similarly, from the point d, we are dropping another perpendicular on the diffracted beam as BB. Remember, the angle here is alpha n. So now, between these 2 parallel beams with unit vectors S 0 for the incident beam and S for the diffracted beam the path difference is equal to A B minus C D right. And, to have a diffraction coming out of these 2 spots 2 atom positions located at A and D, this path difference should be integral multiple of wavelength and when we are talking about this in terms of in the direction of x axis, we term it as n x into lambda.

So now, by simple geometric means we would we can write the path difference where A B is equal to a dot S and C D is equal nothing but a dot S 0 in vector notations. So, we can write this path difference equal to A B minus C D as a cos alpha n minus cos alpha 0 where alpha n and alpha 0 are the angle of diffracted beam with respect to x and alpha 0 is the angle of the incident beam with respect to x. So, the same can be retained in vector notation as a into S minus S 0 which is equal to n x lambda.

So, what does it mean? It means that, if we have a set of points along the x axis and one such point is irradiated with an X ray of unit vector S 0, the direction at which the beam gets diffracted makes a cone of a fixed angle. So, when we have the incident radiation coming at an angle alpha 0, it makes a cone with the angle alpha n for a diffraction and this is true.

Now, in case of all the 3 directions, so, what happens is that the X ray diffraction happens in along a cone with respect to a particular direction. So, in the same manner, what we can write are 3 equations; one is a cos alpha n minus cos alpha 0 equal to n x lambda.

Similarly, we can write for y axis b cos beta n minus cos beta 0 equal to n y lambda and c cos gamma n minus cos gamma 0 equal to n z lambda. These 3 equations are together called the 3 Laue's equations of X ray diffraction which eventually means that the X rays are being diffracted by all the points along x y and z.

And the incident radiation falls in a particular angle with respect to those axis x y and z and gets diffracted along a cone in all the 3 directions. So, it means along cones in every direction which actually means the X ray beam that falls on the crystal diffracts X ray in all the directions as a cone like this which actually means that it diffracts in a spherical manner.

So, this is how the Laue's understanding improved the theory of X ray diffraction and we got 3 Laue equations, but you see these 3 equations are indicating that the directions are to be thought about and then this becomes a cumbersome process to understand diffraction.

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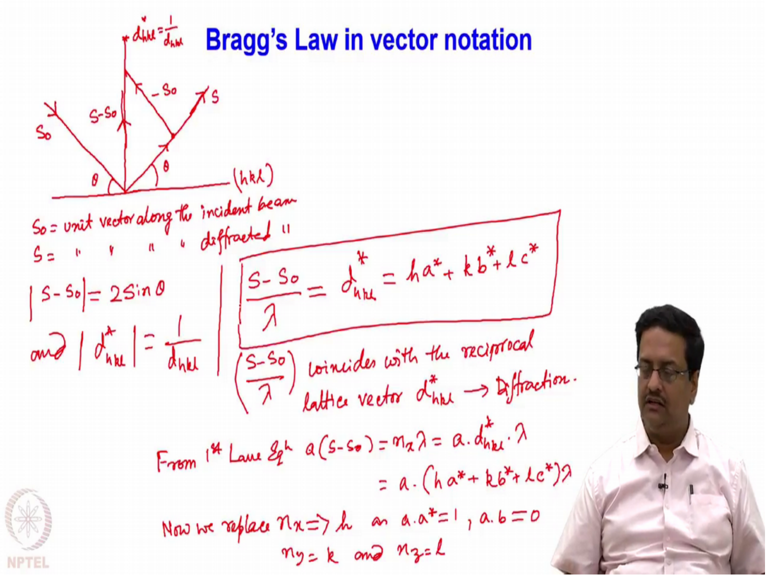

**Bragg's Law in vector notation**

$S_0$ = unit vector along the incident beam
$S$ = " " " " diffracted "

$|S - S_0| = 2\sin\theta$

and $|d^*_{hkl}| = \frac{1}{d_{hkl}}$

$$\boxed{\frac{S - S_0}{\lambda} = d^*_{hkl} = ha^* + kb^* + lc^*}$$

$\left(\frac{S - S_0}{\lambda}\right)$ coincides with the reciprocal lattice vector $d^*_{hkl} \rightarrow$ Diffraction.

From 1st Laue Eqn $a(S - S_0) = n_x\lambda = a.d^*_{hkl}.\lambda$
$= a.(ha^* + kb^* + lc^*)\lambda$

Now we replace $n_x \Rightarrow h$ as $a.a^* = 1$, $a.b = 0$
$n_y = k$ and $n_z = l$

That is why we now follow Bragg's laws of Bragg's law of X ray diffraction and let us try to understand the same Bragg's law in vector space or in vector notation. So, in the same manner, let us consider that the X ray diffraction in the concept of Bragg's is taking place from a particular plane in a crystal. So, this is a particular h k l plane and in that plane the X ray beam is incident at an angle of theta and it goes it gets reflected from the same angle in the other direction as theta, if we designate this beam with the unit vector S 0 and then we designate the diffracted beam as unit vector S.

So, if we draw a perpendicular on this particular plane and cut that perpendicular at d star h k l that is at 1 by d h k l distance; that is the inter planar spacing of this particular plane and then considering this unit vector coming here and then we draw a parallel of unit vector S 0 in the opposite direction and draw it as minus S 0. So, the unit vector the vector here is nothing but S minus S 0.

So, what we have once again is S 0 is the unit vector. Along the incident beam, S is the unit vector along the diffracted beam and we have drawn a perpendicular on the plane h k l which goes upwards like this and we chop it at a distance d star h k l, which is equal to 1 by d h k l.

So now, if you compare the modulus of the vector S minus S 0, that is we consider the modulus of these vector is equal to 2 sin theta and modulus of d star h k l is equal to 1 by d h k l. So, these 2 conditions if we compare and then if we want to take a ratio of the 2 equations, what we end up is the expression S minus S 0 by lambda is equal to d star h k l which is from Bragg's law and this d star h k l can also be written as h a star plus k b star plus l c star where a star b star and c star are unit vectors in the reciprocal space along x y and z.

So, when a constructive interference happens, the Bragg's law or Bragg's condition is satisfied and then we get a diffraction; that is when the vector S minus is 0 by lambda coincides with the reciprocal lattice vector d star h k l , we observe diffraction. So, from the first Laue equation, we can write a into S minus S 0 as equal to n x lambda equal to a dot b h k l star into lambda, which is equal to a dot h a star plus k b star plus l c star lambda.

So now, we replace n x by h as a dot a star is equal to 1 and a dot b is equal to 0. So, similarly we can write n y equal to k and n z equal to l. So, this is how one can convert Bragg's law in vector notation and we can write the Bragg's law in vector form as S minus S 0 by lambda equal to d star h k l equal to h a star plus k b star plus l c star.

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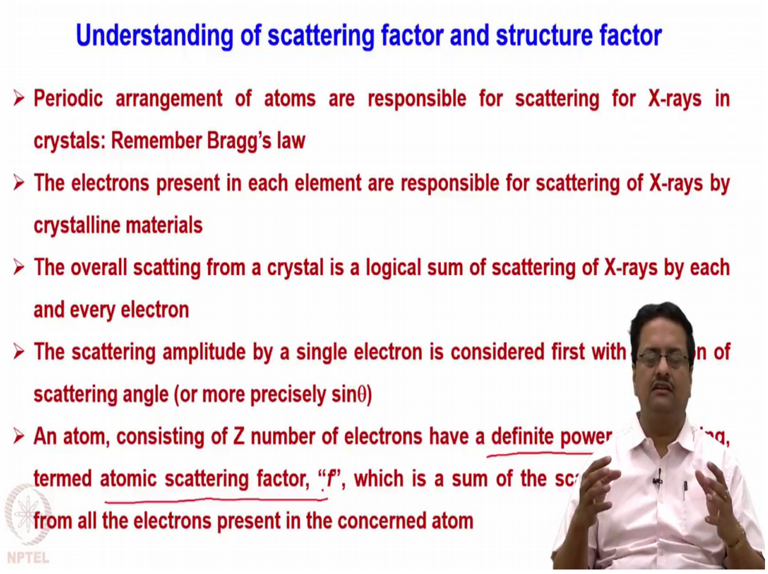

### Understanding of scattering factor and structure factor

- Periodic arrangement of atoms are responsible for scattering for X-rays in crystals: Remember Bragg's law
- The electrons present in each element are responsible for scattering of X-rays by crystalline materials
- The overall scatting from a crystal is a logical sum of scattering of X-rays by each and every electron
- The scattering amplitude by a single electron is considered first with n of scattering angle (or more precisely sinθ)
- An atom, consisting of Z number of electrons have a definite power ng, termed atomic scattering factor, "f", which is a sum of the sc from all the electrons present in the concerned atom

So now, when we are trying to understand how the scattering of X rays takes place from a crystalline material, we need to understand the phenomena from inside. See, when we have periodic arrangement of atoms and we believe that periodic arrangement of atoms are responsible for scattering of X rays in case of crystals and we have derived Bragg's law. And with this understanding, it actually means that the electrons present in each element are responsible for scattering of X rays.

In case of crystalline materials and the overall scattering from the crystal is a logical sum of scattering of X rays by each and every electron representing that. So, the scattering amplitude by a single electron is considered first with the variation of scattering angle and the scattering angle is more easily understood when we do the calculation using sin theta. So, in my next representations, when we talk about scattering angle, we will represent it in terms of sin theta.

And then, when we have one particular atom having Z number of electrons and that is the atomic number of that particular atom consisting of Z number of electrons, they have definite power of scattering that definite power of scattering of each and every atom is called the corresponding atomic scattering factor designated by the lowercase letter f which is actually a logical sum of scattering amplitude from the electrons from all the electrons present in the concerned atom.

So, what is happening? Every electron is responsible for scattering X rays and then when we have a set of electrons for one particular atom, all those electrons the scattering coming from all those electrons are considered to be the scattering power of that particular element.

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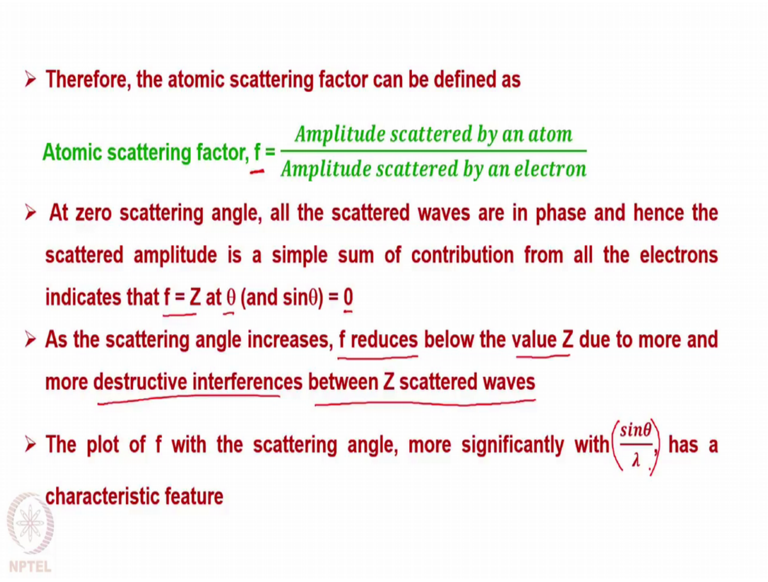

- Therefore, the atomic scattering factor can be defined as

$$\text{Atomic scattering factor, } f = \frac{\textit{Amplitude scattered by an atom}}{\textit{Amplitude scattered by an electron}}$$

- At zero scattering angle, all the scattered waves are in phase and hence the scattered amplitude is a simple sum of contribution from all the electrons indicates that $f = Z$ at $\theta$ (and $\sin\theta$) = 0
- As the scattering angle increases, f reduces below the value Z due to more and more destructive interferences between Z scattered waves
- The plot of f with the scattering angle, more significantly with $\left(\frac{\sin\theta}{\lambda}\right)$ has a characteristic feature

So, the atomic scattering factor can be defined as the amplitude scattered by an atom; that is the amplitude of X ray scattered by an atom divided by the amplitude of X ray scattered by an electron and is if it is designated by the lowercase letter f at 0 scattering angle, all the scattered waves are in phase. And hence, the scattered amplitude is the simple sum of contribution of all the electrons that indicates the f is equal to Z at theta equal to 0 or sin theta equal to 0.

But, what happens? When the scattering angle increases, the phenomena becomes more difficult. More the phenomena becomes different and the scattering of X rays from these atoms changes significantly with change in the scattering angle. So, as the scattering angle increases, f reduces below the value of Z due to due to more and more destructive interferences between Z scattered waves.

So, when we have higher scattering angle, the value of f goes below the value of Z due to more and more destructive interferences between the Z number of scattered waves from each and every electron. So, the plot of this scattering factor f with the scattering angle. More significantly, we represent it in terms of sin theta by lambda has a characteristic feature which I am going to draw in the next slide.

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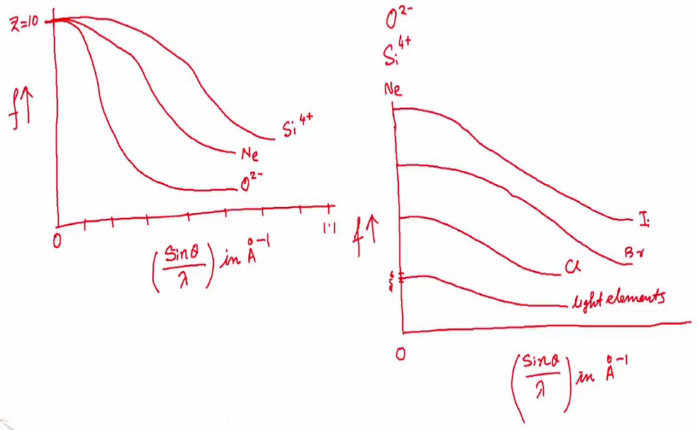
Variation of atomic scattering factor



The scattering factor f is represented along y; remember the scattering factor corresponds to the atomic number Z n. And, if we try to plot sin theta by lambda in x axis, remember lambda is represented in angstroms. So, 1 by lambda is being represented in angstrom unit angstrom inverse unit. So, the unit along x axis is angstrom inverse and at sin theta, theta equal to 0, sin theta is 0 and theta equal to 90-degree sin theta is 1 and then 1 by wavelength which is in case of molybdenum can be 0.77 angstrom in case of copper can be 0.54 angstrom.

So, depending on the wavelength, this axis will be spanned either below 1 or up to 1. So, we can have values like this. Suppose, I am plotting it up to 1.1, using copper radiates of a using molybdenum radiation. So now, for oxide iron O 2 minus iron, which has 10 electrons in it, the scattering factor behaves like this. This scattering from this oxide anion reduces very rapidly with respect to sin theta by lambda.

If we consider another isoelectronic species which is silicon 4 plus which also has same number of electrons, but much more number of protons the scattering factor falls like this if we draw the same plot for the inert gas neon which also has 10 electrons. So, it starts from here and falls like that all these are starting from Z equal to 10.

So, this in to the nature indicates that the scattering factor for all the atoms with a particular value of Z starts from the same point and then deviates in a different way. Why is it like that? In case of Si 4 plus, the nuclear charge is much higher. As a result, it can bound bind the electrons around it more tightly towards it; as a result, the electrons are more closely associated with the atom itself.

Hence, it is scattering power does not reduce very fast as it happens in case of oxide where the nuclear charge is much less compared to silicon. And as a result, the nuclei nucleus do not have significant hold on the electrons and the electron cloud for oxide is much more diffused compared to the electron cloud around the silicon and hence the scattering power of oxygen falls very rapidly.

So, this is how the scattering factor changes with the different atoms. Let us see if we have atoms with very much different atomic numbers. What happens to the value of f? If we try to plot f with sin theta by lambda for different atoms, once again in angstrom universe unit most of the organic compounds contain light elements; that means, carbon nitrogen oxygen sulphur etcetera.

So, carbon nitrogen oxygen they have atomic numbers very close 4 5 6 etcetera. So, those elements decay very quickly. The scattering factor decay very sharp and goes like this. So, this I am plotting as light elements of course, these curves are going to be slightly different for carbon nitrogen oxygen and so on. But then, if we compare the same with chlorine which has a larger number of electrons, the plot goes like that for bromine. It is much higher and diffracts up to much higher angle and if we have iodine with a large atomic number, the atomic scattering factor falls like that.

So, this is how the scattering factor for various atoms varies with the angle of diffraction that is sin theta by lambda. And that is why, the compounds which has heavier elements. They diffracts better at higher angle with in comparison the compounds, which are having only light atoms like organic small organic molecules which are having only carbon hydrogen nitrogen and oxygen they diffract less. Whereas, if you have bromine or the chlorine or iodine in your molecule, the crystals containing such molecules diffract better because you have a better scattering from the heavier element.

So, in today's lecture, we understood the representation of Laue's and Bragg's equations in the vector notation. Then, we have tried to understand the theory behind scattering of X rays by different elements, what are the factors that influences the scattering for different elements and we got to know about a new term called the scattering factor or atomic scattering factor which varies with the scattering angle. So, in the next class, we will continue this topic.