

ELEMENTS OF MODERN PHYSICS

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Lec 23: Crystal Structure, Bragg's Law

We shall be starting a new module called as the solid state physics and in solid state physics we will be doing a few important topics and that are relevant for these learning of physics or this modern physics that the course aims for and in this we will talk about in this lecture we will talk about crystal lattices in particular we will talk about Wigner seitz cell conventional unit cell, coordination number, some crystal structures, and specifically some of the popular structures that we come across, Bravais lattice and some special crystal lattices. Then we'll talk about reciprocal lattice, Miller indices. and how these crystal structures are determined using X-ray diffraction. Then we talk about Bragg's law and an alternate formalism, which is known as a Von Laue formalism.

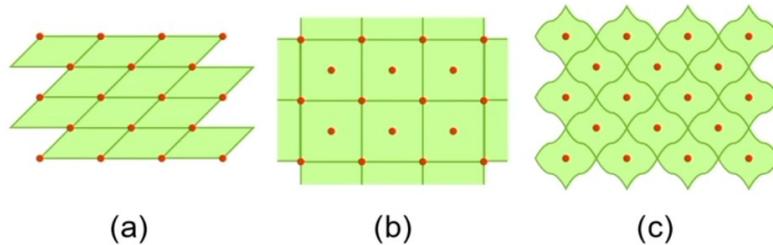
We'll talk about structure factors and the selection rules which are specific to the lattices, the crystal lattices, the type of crystal lattice that which order or which peak will survive and which peak will not. That is given by the selection rules. So we'll talk about that. So let's start with the definition of a unit cell. So unit cell is the repetitive arrangement of the smallest unit, which is capable of building up the entire crystal structure.

So if you take one unit cell and then replicate it in all directions, say x-direction, y-direction, and z-direction, that would give you the entire crystal structure. That's called as a unit cell, the smallest one of that. For example, these unit cells are shown by the corners of these red dots. So each of them is a unit cell. So that when translated along the coordinate axis, they produce the entire crystal structure.

And that's what is shown in all of A, B, and C. So these are a variety of these unit cells that are there. And this figure is taken from this website. A primitive cell, on the other hand, is a unit cell that contains only one lattice point. So that's the smallest possible structure of a crystal lattice. If you take an example, if there's a lattice point that lies at the edge of a unit cell, then it's shared by another adjacent similar unit cell, then it's only counted half.

Unit Cell

Repetitive arrangement of smallest units, which are called as **Unit cells** build up the build up the crystal structure. Translating a particular unit cell produces the entire structure.



A variety of unit cells are possible for a given crystal structure.

Accordingly, a lattice point located at the corner of a cube We're talking about in three dimension is shared by eight such cubes. So we talk about a primitive unit cell or a primitive cell. A primitive cell is a unit cell that contains only one lattice point and is the smallest possible structure of a crystal lattice. Now, suppose there is a lattice point that lies at the edge of a cell, we just talked about say two dimensions, and is now shared by say with another similar unit cell.

Then it's only counted as half. So one point is being shared by two unit cells and it's counted as half. So for example, in 3D, if you talk about a cube, lattice point that's lying at the corner of the cube is actually shared by eight such cubes. And so it will be counted as one-eighth. So let's talk about a Wigner-Seitz cell.

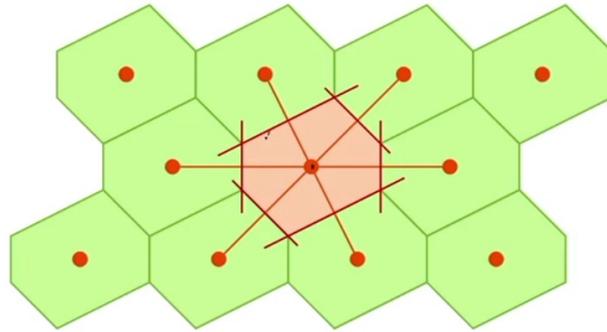
These are special primitive cells which are known as Wigner-Seitz cells. And the primitive unit cell of a Bravais lattice is called a Wigner-Seitz cell. And how can it be constructed? It can be constructed by taking a particular point and joining it with all other nearest neighboring points. And then you take a perpendicular bisector of all these connecting lines, and the volume it encloses is called a Wigner-Seitz cell.

OK, so that's the definition of a Wigner-Seitz cell. Let's just go over it for clarity once more. So you take a particular point and then you join it with all other neighboring points

that are nearest neighbors. And then you draw a perpendicular bisector. And these perpendicular bisectors from all sides will enclose a volume, and that volume is what we know as the Wigner-Seitz cell.

So, there are 14 Bravais lattices and 230 non-Bravais lattices. So, some of these are pure information. So, let us you know see this more carefully I mean this or rather construction of a Wigner-Seitz cell. So, you see that there is a red point that you see here and that is connected to all its neighbors in say a honeycomb kind of lattice and these are the six neighbors that you see there. So, they are connected now—this is in 2D.

Construction of Wigner Seitz Cell.



So, you take the perpendicular bisector of each of these lines. And the volume that it encloses—in this case, it is an area—this is a Wigner-Seitz cell. What are reciprocal lattice vectors? In fact, this is an important concept that pervades all of solid-state physics, to be particular. We go to a Fourier space; sometimes, we prefer talking about Fourier space.

Because Fourier space is more convenient to talk about. That's because the real space has a finite extent. You cannot really consider an infinite real-space lattice. You can always consider or visualize that. But for any calculations, we have to think of extending it in all directions, from minus infinity to plus infinity.

Whereas, in the reciprocal space or in the Fourier space, it is much easier to talk about the k vectors. And these, you know, the k vectors are defined as k equal to, you know, these

wave vectors, these are k equal to 2π over λ . So, in principle these infiniteness of the space is encoded in the k space where you know the smallest k vectors actually correspond to large λ , very large λ , infinite λ which means that it can accommodate you know wavelengths which are or waves which have a very large wavelengths. So we define these unit cells. So, these A_1, A_2, A_3 are the primitive vectors of the crystal lattice in real space.

So you can write that in real space. And let us define B_1, B_2, B_3 as the primitive vectors of the reciprocal space. Okay. And we have this equation 1 and each vector, which is B_1, B_2, B_3 . is orthogonal to a_1, a_2, a_3 , and then they have this relation where $b_i \cdot a_j$ equals $2\pi \delta_{ij}$.

What it means is that this δ_{ij} is called as a Kronecker delta which is equal to 1 for i equal to j and is equal to 0 for i not equal to j . Which means that $B_i \cdot A_i$ would be 2π or $B_1 \cdot A_1$ would be 2π and so on. $B_2 \cdot A_2$ will be 2π . If you take a dot product or the inner product with B_1 and A_2 , that would be 0. That is what according to this definition.

Reciprocal lattice Vectors

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\underbrace{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}_{\text{Volume}}}; \quad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}; \quad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}. \quad (1)$$

(direct) in real space

With $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ are primitive vectors of the crystal lattice, then $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ are primitive vectors of the reciprocal lattice. Each vector defined by (1) is orthogonal to two axis vectors of the crystal lattice. Thus $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ have the property

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij},$$

$$\delta_{ij} = 1 \text{ for } i=j$$

$$= 0 \text{ for } i \neq j$$

A proper reciprocal lattice vector \mathbf{G} is formed out of the \mathbf{b} vectors,
 $\mathbf{G} = p\mathbf{b}_1 + q\mathbf{b}_2 + r\mathbf{b}_3$ with p, q and r are integers.

And we also define a reciprocal lattice vector, which is formed out of these B vectors. In fact, this reciprocal lattice vector G plays a very important role in our analysis of crystal

diffraction or Bragg diffraction. This is formed out of these b vectors where G is defined as $p b_1 + q b_2 + r b_3$ where P, Q, R are integers. So, this has all the definitions that we require. We require definitions of the unit cells, such as the primitive unit cell, the Wigner-Seitz cell, and these direct lattice vectors.

So, a_1, a_2, a_3 are also called as a direct lattice vectors. So, they are the vectors in the real space, and b_1, b_2, b_3 are the vectors—primitive vectors in the reciprocal space. They can be obtained from a 's by these relations of b_1 equal to 2π into $a_2 \times a_3$ divided by $a_1 \cdot a_2 \times a_3$ and similarly b_2 would be $a_3 \times a_1$ divided by the same quantity and $a_1 \times a_2$ for b_3 and divided by the quantity and this is the volume in the real space. That is basically the volume that is made out of the three vectors a_1, a_2, a_3 in the real space.

<p>CUBIC $a = b = c$ $\alpha = \beta = \gamma = 90^\circ$</p>	
<p>TETRAGONAL $a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$</p>	
<p>ORTHORHOMBIC $a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$</p>	
<p>HEXAGONAL $a = b \neq c$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$</p>	<p>TRIGONAL $a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$</p>
<p>MONOCLINIC $a \neq b \neq c$ $\alpha = \gamma = 90^\circ$ $\beta \neq 120^\circ$</p>	
<p>TRICLINIC $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$</p>	

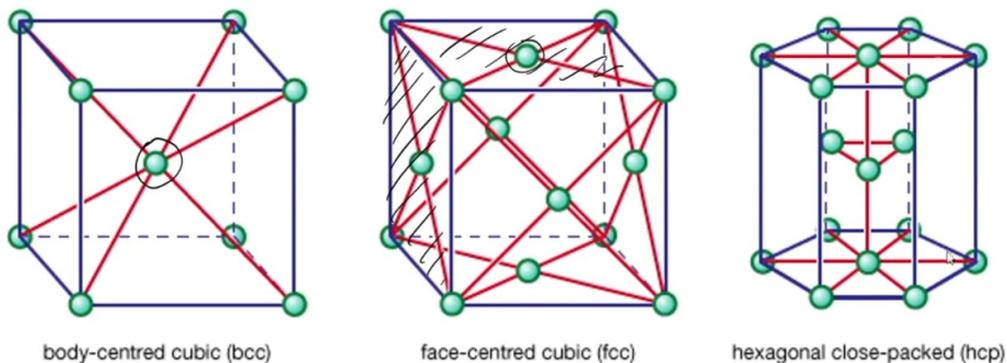
4 Types of Unit Cell
 P = Primitive
 I = Body-Centred
 F = Face-Centred
 C = Side-Centred
 +
7 Crystal Classes
 → **14 Bravais Lattices**

And so if you take this volume to be just a number, so b_1 equal to 2π over V $a_2 \times a_3$ and that is why this orthogonality relation between the reciprocal lattice vectors and the direct lattice vectors take place. So, let us see certain crystal lattices or just a generic form for the crystal lattices and they are cubic where you know α, β, γ are the angles between a, b and c vectors. these are all equal to 90 degree and a equal to b equal

to c that is called as a cubic the simplest one and then we have tetragonal systems where a equal to b but not equal to c so two of them equal but the third one is not equal yet they are the angles are still 90 degree orthorhombic means that none of them are equal so we have a you know a cubic lattice with no sides a not equal to b not equal to c Angles are still 90 degree and hexagonal lattice has A equal to B but not equal to C . Two of the angles are 90 degree but one is 120 degree. Similarly, we have a trigonal where A equal to B equal to C but the angles are not 90 degree.

We have monoclinic which none of the sides are equal but we have these α equal to γ equal to 90 and β equal to be not to be equal to 120, which means that is the difference between the hexagonal and the monoclinic. Of course, there is also a difference in the direct lattice vectors, which are A . So, remember this A , B , C are the distances or the lattice spacing in the X , Y and Z directions and then there are triclinic and so on. So, there are 14 types of unit cell, P is called as a primitive, I is the body centered, F is face centered, C is side centered which are all written here with P , I , C and so on and plus you have 7 crystal classes as said earlier and there are 14 kinds of Bravais lattices. So, this common structures that we encounter there are these cubic structure where it is a body centered cubic other than this simple cubic which has only 8 atoms at the corners at the vertices of a cube.

Common metallic crystal structures



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This has one more atom at the center at the body center that is called as a body centered cubic and then there is also a face centered cubic which every face has at the center of every face. So this is that face which is side face. So, that is on the left side face, there is an atom there, there is an atom on the top face that you see here and so on. So, that is

called as a face center. So, all of these six faces that we come across which are front, back, left, right, top, bottom, all six have one atom at the center.

Then there are hexagonal close packs, which has these kind of a structure, which has, you know, a hexagonal structure at the base and at the top. And then there's a triangular structure at the midpoint of this six sided figure that you're seeing. So some of these crystal structures are this NaCl structure and these cesium chloride structure, the diamond structure and the zinc blend structure. So let me tell you about this Cl structure. You can still see that these are in the NaCl.

These are by this closed black dots and that there are open white dots. The open white dots are called as the sodium plus sodium. and this is Cl minus and similarly we have also Cs plus and Cl minus we have diamond and zinc blend which have essentially the same structure and let us just discuss this structure so Cl atoms are there in this NaCl at 0 0 0 and then it is half half 0 I will write it without So these are the coordinates of that and then we have half, zero, half and we have zero, half, half. So these are the chlorine atoms.

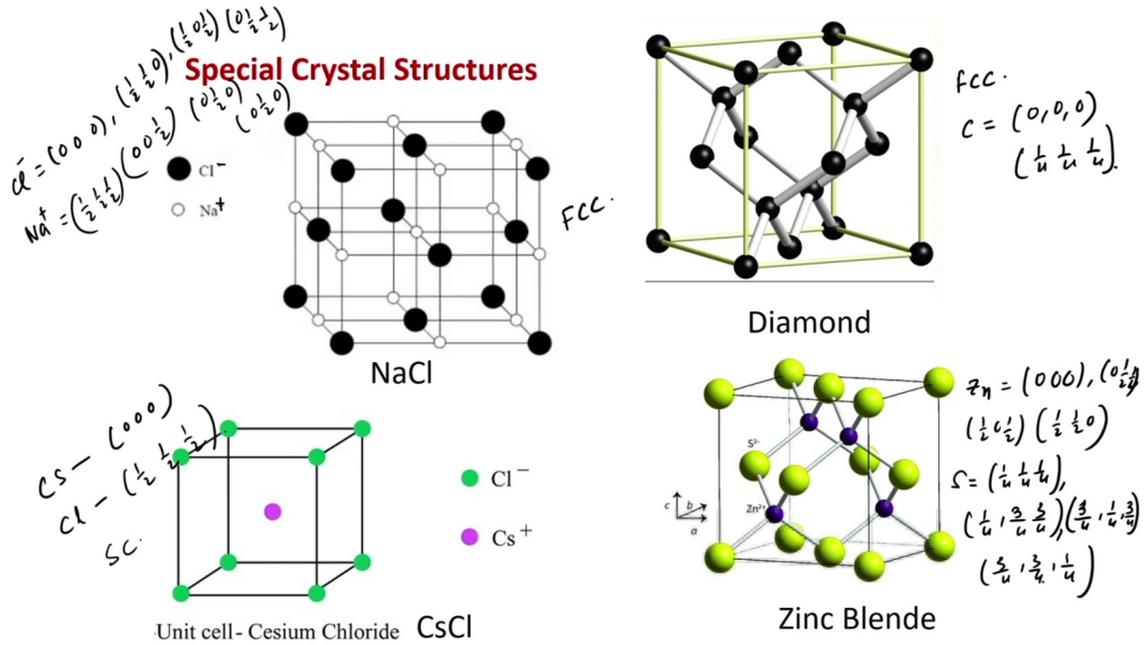
So chlorine minus is situated there and the sodium atoms are situated at half, half, half and then we have zero, zero, half. And we have zero half zero. And then we have zero half zero and so on. OK. It's getting a little cluttered, but I think you can figure it out that where this chlorine and the sodium ions are.

And for this, we have this is, you know, FCC structure. And this is a simple cubic structure. The unit cell is actually simple cubic structure. So, Cs is at 0, 0, 0 and the Cl minus atoms are at half, half, half, okay. So, each atom must be viewed as at the center of this cube of atoms of the other kind that is Cs is in this body centered position for the Cl atoms and so on, okay.

And let us see the diamond structures. The diamond structure we have the carbon atoms are there in there are so this again this is an FCC structure. This is a simple cubic structure. This is a FCC structure with this carbon atoms at 0 0 0 and they are at one fourth one fourth and one fourth. So these are two atoms per unit cell.

You see a lot of atoms but they are shared by other neighboring cubes. And for the zinc sulfide, which has essentially the same structure, we have zinc to be equal to at 0, 0, 0, then we have it at 0, half, half and then we have it at half, 0, half and then we have half, half, 0 and the zinc and for the sulfur, we have one fourth one fourth and one fourth. And we have one fourth, three fourth, three fourth, and we have one three fourth, one fourth,

one fourth, or one fourth. and then we have 3, 4, 3, 4, 1, 4, okay. So, that is the zinc and the sulfur atoms are situated, okay.



So, these are some of these common crystal structure and sodium chloride is nothing but the salt that you eat and And so how do we know the crystal structures? I mean, how do, how have one, you know, found out that how people have determined these crystal structures to be FCC and with these, you know, carbon atoms to be placed there, carbon, these are all carbon atoms for diamond, whereas zinc sulfide, even though they are the same structure, but they are two different atoms there. How do we know all that?

And that is known by this X-ray diffraction technique. And before we go on to that, the reason that X-rays are employed to determine the crystal structure is that the wavelength of the X-rays are of the order of angstroms and this lattice spacing in general are of the order of angstroms as well. So, this forms a natural probe for this determination of the crystal structure because if you have the wavelength to be too large, then you will be missing the atoms in between and if you have it too small, then you will not see the atoms where they are located. So, ideally one should use a probe which is of the same order as the measurement that you intend to make. So, you see that there are periodic arrangements of atoms that are placed there.

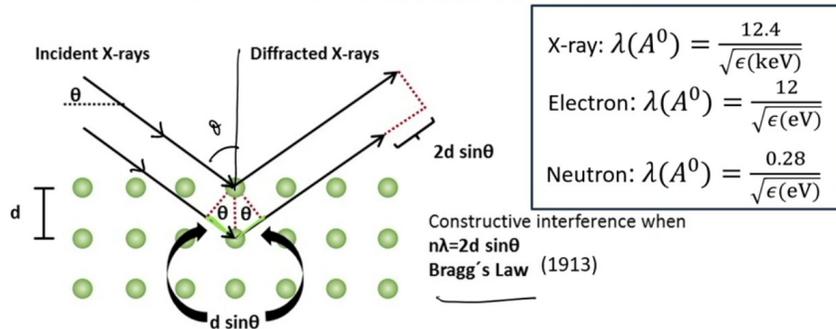
And there is an incident X-ray that falls on these two neighboring planes that we show here. These neighboring planes are shown by these green dots or green balls that are there, which are nothing but the lattice points. And then the X-rays are diffracted from these green dots that you see there. And so the angle that you have is really the angle with, you know, this angle with the normal. and if there is the vertical distance between the planes that is the green dots is D then you have these lengths let me show it by a color that these lengths are of you know of $D \sin \theta$ and so the phase difference or rather the path difference that these diffracted X-rays pick up because of diffracting from different

planes of the crystal is nothing but $2D \sin \theta$. So from this theory of interference, it says that if the path difference becomes $2D \sin \theta$, if it matches with integer times the wavelength of the X-rays or whatever probe you are using in this particular case, it's X-rays. So, λ is the wavelength of the X-ray. So, if $2D \sin \theta$ matches $N \lambda$, where N is a certain order— N can be 1 or N can be 2, N is just an integer. If it is integer times λ , which is the wavelength of the probing wave, then we get constructive interference.

And this constructive interference will give a peak in the output. We are just going to see that. And this is known as Bragg's law. This is known as Bragg's law, and Bragg actually found it in 1913. So, typical interatomic distances are of the order of an angstrom.

So, any probe must have a wavelength of that order. Okay. So, This is what we have said. And for X-rays, we have, you know, E equal to the energy of the X-rays, which is $h \omega$, or hc / λ .

Determination of Crystal Structure: X-ray Diffraction



Typical interatomic distances are of the order of an Angstrom. Any probe must have a wavelength of that order.

$$\text{For X-rays, } E = \hbar\omega = \frac{hc}{\lambda} = 12.3 \times 10^3 \text{ eV for } \lambda = 10^{-8} \text{ cm}$$

These are characteristic X-ray energies.

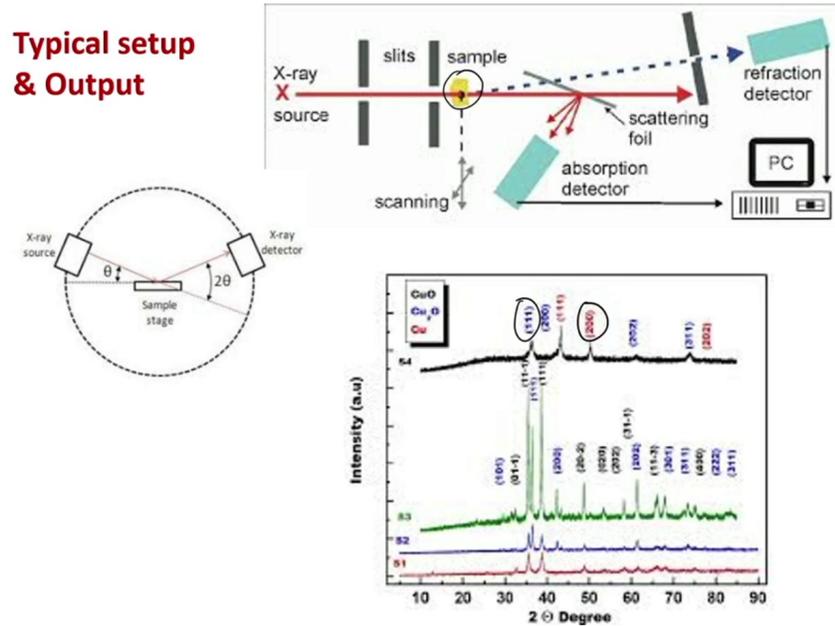
And if you put in all these values and these are for lambda equal to, you know, 1 angstrom, we have these energies to be equal to some 10 to the power 4 electron volt approximately. And these are characteristic X-rays and that is why they are suitable for determination of the crystal structure. We'll be right back. So this is a typical setup of this X-ray diffraction. So X-ray, there is an X-ray source and it goes through some slit and it falls on the sample, which is a crystal lattice.

And from there, it falls on a screen. And then, of course, the screen is. So there is also a scattering foil that is there. And from the scattering foil, it gets absorbed into the detector and the detector sensitive PC. your computer for analysis of data.

So, a more you know simple and schematic diagram would be that there is an X-ray source which comes and falls on the sample and this gets you know diffracted and there is a detector that is placed here on the right and there is an angle 2θ So that's called as the angle of these or the diffraction angle. And one actually measures or rather plots the intensity of these X-rays that are detected by the detector after being diffracted by the sample. And one usually sees all these differences. Peaks that you see there, there are of course some noises, but these prominent peaks are sort of mapped onto certain numbers.

As you see, it is a little vague, but you can see these 111 and some 200 and all that. So, these are done on some copper oxide and one gets this X-ray diffraction. It can be done on any X-ray. any sort of crystal structure and that gives the determination or rather

information about what are the coordinates of this copper atom, what are the coordinates of this oxygen and so on so forth, okay. And as you see that it is plotted as a function of 2 theta, where 2 theta is the diffraction angle that you see there on the diagram on the left.



Okay, so the Bragg's law gives a condition for the constructive interference for the X-rays, which are scattered from different planes of the crystal, which is what we have seen. $2D \sin \theta = n \lambda$ is Bragg's equation. It is a fairly simple enough equation for us to analyze. So, you would be knowing everything excepting one parameter, and this D is actually related to the HKL indices. This D is related not only to the HKL indices, which are called Miller indices—we are going to see that—but it also depends on the lattice spacing, and that depends on the crystal lattice as well.

λ , as we have said, is the wavelength of the X-rays. D is the interplanar spacing. We have seen that. 2θ is the angle of scattering, and θ is the incident angle with respect to the normal. n is the order of the pattern.

So, how do we find out these Miller indices? The intensity of these X-rays, which we will discuss later, along with some selection rules. It depends on how many atoms per unit area are there who are taking part in the scattering process. Interplanar spacings and how many planes are involved, etc. And these planes are given by this Miller indices.

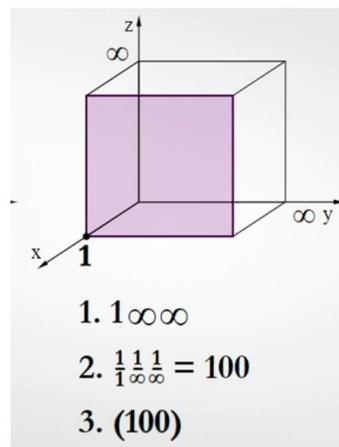
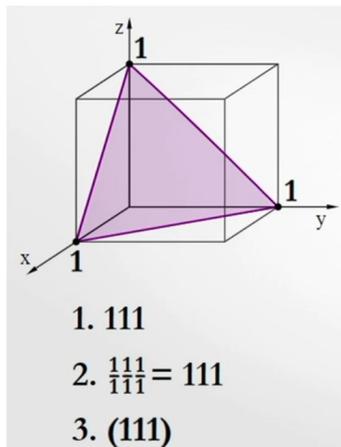
And what are these Miller indices? These are denoted by $h\ k\ l$. And they are, you know, determined by—pardon me for the spelling mistake—determined by the following things. So, you determine the intercepts of the plane. along the crystallographic axis in terms of the unit cell dimensions.

I will give you example of that. Then take the reciprocals, then clear the fractions which means that you sort of remove the fractions and then reduce it to the lowest terms such that they are integer and we get this plane. Just now you saw that the output has $1\ 0\ 0\ 2\ 0\ 0$ and so on so forth. So, this is how these $h\ k\ l$ or the Miller indices are determined. We show some very simple planes.

So, there is a cube that you see and the plane that you see which is, you know, colored in this magenta color is the 111 plane. So, what we did is that we found out this plane. The intercepts, which is $1, 1, 1$ along X, Y and Z directions, then you make these as fractions in terms of this. So, this is a unit cube. So, the fraction is 1 by $1, 1$ by 1 and 1 by 1 .

So, that becomes $1, 1, 1$. The plane is $1, 1, 1$. So, the crystal plane that you see here, which is painted in this magenta color is a $1, 1, 1$ plane. For example, see another plane, which is, you know, has it's only the phase that's coming out. So this has, you know, in the X direction, it has a projection or it is distance from the center is one unit.

Finding Miller indices on a unit cube



Now, this is only the plane that is facing you. So, it has Y to be infinity and Z to be infinity as well. So, this plane can actually go anywhere from 0 to infinity in the Y and Z directions. So, we take the reciprocals: it is 1 by 1, and then 1 by infinity, 1 by infinity; we get 1 0 0. So, again, the magenta-colored plane that you see is the plane.

Let me show you maybe one or two more, and let me sort of draw it here. So, this is a cube that you have. And let us take this plane, the plane that you see here. Let me highlight this plane. So, this is the plane that we are trying to find out.

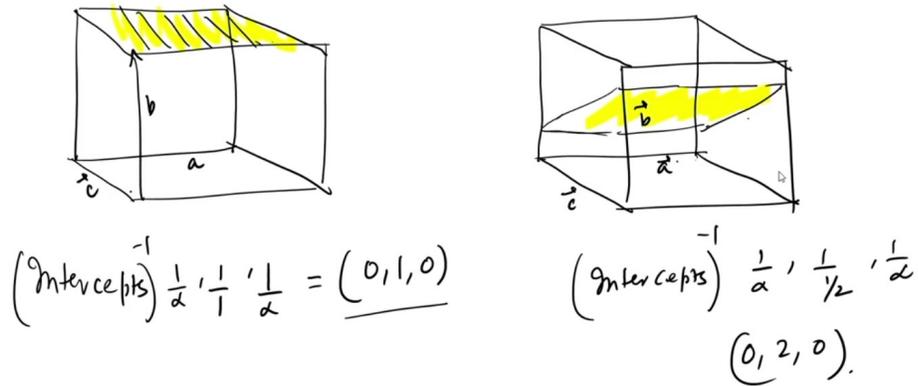
And how do we find that out? So, the intercepts are 1 by infinity, 1 by infinity—that is the plane that is at z equal to 1. So, this is z equal to 1, and this is—sorry—this is y equal to 1. So, this is y equal to 1.

So, your A is in this direction, and B is in this direction. So, that is in the direction of B . And this is the C direction. So, this is how we have defined it. So, this is 1 by infinity, 1 by 1, and 1 by infinity again.

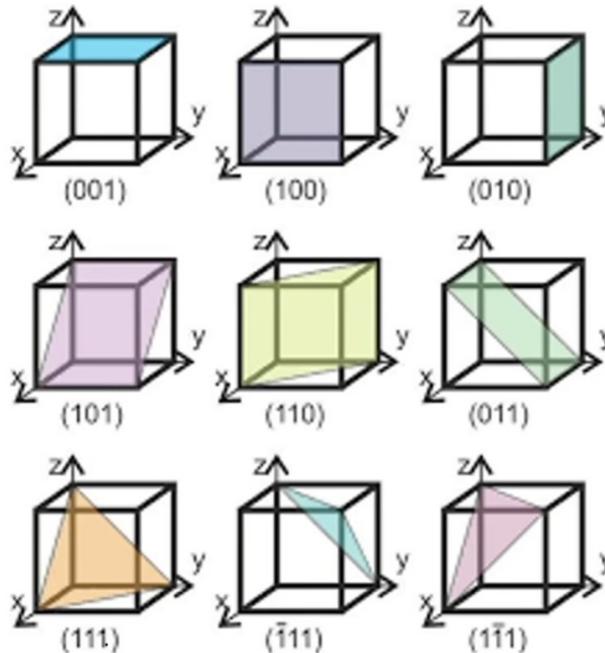
So, what we do is that we sort of take this 0. So, 1 by infinity is 0, and then it is 1, and it is 0. So, this is the 0, 1, 0 plane, and so on and so forth. So, if you take a plane which is at the middle of this, so let me you know draw another one to avoid cluttering on the same.

So, we draw another cube that we see here and once again we call it a B and we call it a you know a C and we call it A okay and suppose this plane that we want to show is basically this plane that is you know is this plane that is there at the you know kind of a by 2 okay so this is at the middle and let me again paint that this is the plane that you want to find out and then this plane is the intercepts are 1 over infinity, 1 over 1 by 2, that is basically the intercepts, so the inverse of the intercepts. So, okay, we write it just once: this is 1 by half, and then it is 1 over infinity. And so, this is a 0, 2, 0 plane, okay.

So, the one that you see there is a 0, 1, 0 plane and the one that is at the middle. So, this is actually in the middle, basically. So, that is at a by 2. You may not have drawn it very well, but this is at the half the distance inside the cube. All right.



So, that is about these Miller indices. We show a large number of them. So, 0, 0, 1 is according to the, you know, the X, Y and Z. We have taken different definitions of X, Y and Z. So, you take the definitions of X, Y and Z according to your wish and then you can form these planes and 1 1 1 we have already seen and some of these other planes we have seen as well. So, these planes are labeled according to the hkl values.



So now we have gotten this hkl and we have also you know wrote down Bragg's law which is $2d \sin \theta = n \lambda$, d is the perpendicular or rather the distance between two planes and the shortest distance basically. And how are these d s related to

hkl and a is the lattice constant which if you take a unit cube then of course a becomes equal to 1 but a is otherwise the distance between nearest neighbor atoms so that is a. So, we have $1/d^2$ equal to $h^2 + k^2 + l^2$ divided by a^2 for a cubic lattice for a tetragonal it is $h^2 + k^2$ by a^2 plus l^2 by c^2 and for hexagonal it has more complicated form and for orthorhombic it has this form okay. So, now if we know these d and a, we can find out these hkl indices, and these hkl indices are noted on the diffraction intensities that you see here, okay.

Relationship between d and (h, k, l)

Cubic:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

Tetragonal:

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

Hexagonal:

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$

Orthorhombic:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

So, these are the hkl planes which are scattering. So, which plane is giving rise to the scattering and which atoms are there all those information we can find out. So, we basically can find out the crystal structure of a given lattice. Now, while we formulated Bragg's law, there is an important assumption that went in and this assumption is that we have sectioned the crystal lattice into different lattice planes and we have looked at the scattering from these planes and these scattered X-rays, they are allowed to interfere. And because they are from different planes, there is a path difference and this path difference will give rise to a phase difference and so on so forth, depending on these path difference to be, you know, having integral multiple of lambda or integral.

Otherwise, we have an interference pattern or a maxima in the interference pattern or rather a constructive interference. But so this sectioning of crystal into lattice planes is

done. So that's an approximation or rather that's a superimposed condition that we have done in order to understand Bragg's law. In addition to that, we have assumed that specular reflection. What is meant by specular reflection?

It is like a mirror-like reflection. We saw that figure in which the incident angle is θ with respect to the normal. And we have the scattering angle to be θ as well. And then that gave rise to these extra path difference of these red dotted lines, which are $d \sin \theta$ and $d \sin \theta$. That gave rise to $2d \sin \theta$.

Assumptions of the Bragg's law:

1. Sectioning of the crystal into lattice planes
2. Specular reflection is assumed

Von Laue formalism:

1. No sectioning of the crystal is done.
2. Crystal assumed to be composed of identical lattice point \vec{R} apart.
3. Each lattice point scatter uniformly in all directions (not mirror-like).
4. Diffraction peaks observed when scattered radiation interfere constructively.

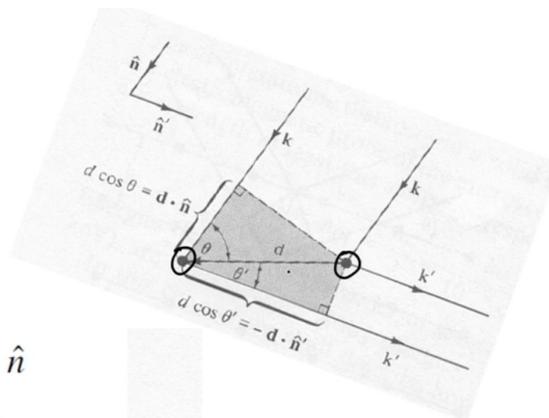
So, these two are the main assumptions of Bragg's law. In fact, there is another formalism called the Von Laue formalism, where no such sectioning of the crystal needs to be done. And we just consider a crystal to be composed of identical lattice points, which are separated by a lattice vector \vec{R} , where lattice vector \vec{R} is nothing but some $p a_1$ plus $q a_2$ plus $r a_3$, where p, q, r are integers. They can also be written as n_1, n_2, n_3 or n, m, l , and so on, okay.

So, that is the definition. So, that is basically when you go from one lattice point to another, it constructs the entire crystal. And so the crystal is just simply we take two points which are at a distance \vec{R} apart and we don't section it into planes and neither specular reflection is assumed. So each lattice point instead of like mirror, it scatters uniformly in all directions, not mirror like. Right.

If you stand in front of a mirror, then only you can see yourself. But if you see the mirror from a side, you do not see your image on the mirror. And that's because the mirror only gives rise to, you know, a kind of reflection where the incident angle and the reflected angle would be same. So there is no mirror like reflection that you see. And that is not required in this particular case.

And the diffraction peaks are observed when the scattered radiation that interferes constructively. That, of course, remains unchanged because you need to have a scattering condition. But the main two assumptions, that is sectioning of the crystals into lattice planes and the specular reflections, these are, you know, waived off. So, we draw a picture we see that there are two lattice planes which are these two ones that you see there these are at a distance r apart or these are at a distance d apart d could be a vector. So, well d could be r or you know we have written that d to be a nearest neighbor distance.

Schematic diagram



Incident x-ray: along direction \hat{n}
wavelength λ
wave vector $\vec{k} = \frac{2\pi}{\lambda} \hat{n}$

scattered wave: direction \hat{n}'
wavelength λ
wave vector $\vec{k}' = \frac{2\pi}{\lambda} \hat{n}'$

$$\vec{d} \cdot (\hat{n} - \hat{n}') = d \cos \theta - d \cos \theta'$$

And an X-ray comes. Okay. So, this is the direction of the incident X-ray, which is k . And let us call that the n -cap direction. That unit vector is the n -cap direction. And there is another X-ray which is coming and falling.

X-ray means the X-rays are incident on these two points. And they are getting scattered in this direction and that direction from these two points. And they have K prime. So, that is the wave vector because it is a vector. So, these incident X-rays are in the direction of \hat{n} , and the scattered X-rays are in the direction of K .

n cap prime and what you have is that this distance is like the horizontal distance which is shown by this under brace is the $d \cos \theta$ prime which is nothing but a minus $d \cdot \hat{n}$ cap dash. So, that is the n cap prime direction and so incident x ray is along n cap direction wavelength is λ k equal to 2π over λ into n cap Scattered wave direction is n cap. Again, wavelength does not change. So, that says that your K and K prime, the magnitude of them are equal.

Both are 2π over λ , but vectorially they are different because \hat{n} cap points in different directions. And so, $d \cdot \hat{n}$ cap minus n cap prime which is $d \cos \theta$ plus $d \cos \theta$ prime where d is shown there. So, if you actually draw a vector from this one lattice point to another lattice point, we go to this that vector connecting the two lattice points is equal to d . So, no sectioning of planes is done and there is no specular or mirror like reflection has been assumed. So the condition for constructive interference is that these $d \cdot \hat{n}$ cap minus n cap prime, which is basically nothing but, you know, the $d \cos \theta$ plus $d \cos \theta$ prime. That path difference has to match with $m \lambda$.

Here we have written m . m is just an integer. We had written n earlier, but they mean the same thing. So, what we do is that you multiply it by 2π both sides, and that gives rise to, you know, this equation, which is $d \cdot k$ minus k prime, which is equal to $2\pi m$. So, k is equal to 2π over λ . So, we multiply it by 2π and absorb this λ on the left-hand side. So, these k minus k prime dot r . So, d is nothing but r , basically.

R is a direct lattice vector. Which we have written as D . Why have we written it as D to begin with? Because D is arbitrary. D is an arbitrary vector in the real space. It can be a direct lattice vector, which is what we have defined as R . So, because D can be anything, D can be equal to R . Thus, we have this relation: K minus K prime dot R equals $2\pi m$.

That is equivalent, in some sense, to this condition: Bragg's law. We will see that. But the condition that gives rise to this constructive interference—and you should see a peak that is quite different—the condition is quite stringent, as we shall see in just a short while. So, K minus K prime is a valid reciprocal lattice vector, right? Where K is the direction of the incident X-ray and K prime is the direction of the scattered X-ray. And if it is not

equal to this reciprocal lattice vector—remember, the reciprocal lattice vector is defined as (I am writing it again)—let me write it as $n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2 + n_3 \mathbf{b}_3$.

Where n_1, n_2, n_3 are integers. Now, if this is the condition: exponential $i \mathbf{G} \cdot \mathbf{R}$, if \mathbf{G} is a reciprocal lattice vector and \mathbf{R} is a direct lattice vector, then this has to be equal to $2\pi m$. Okay, because this is the condition that comes from the orthogonality of these. So, it comes from this $\mathbf{a}_i \cdot \mathbf{b}_j$ that is equal to $2\pi \delta_{ij}$. Okay.

So, the phase has to be, you know, periodic. If \mathbf{g} and \mathbf{r} , they correspond to the reciprocal lattice vector and the direct lattice vector. So, this tells you that, you know, $\mathbf{G} \cdot \mathbf{R}$ or something or, you know, this is a stringent condition that the change in wave vector has to match a proper reciprocal lattice vector. This is what is coming. But the condition, if you think about it,

X-rays are coming with some their own wavelengths and in a given direction. So, the change in the wave vector of the incoming and the outgoing X-ray or the incident of the scattered X-ray that has to match exactly the reciprocal lattice vector. If that happens, then only there is a constructive interference and you will get a peak in the output spectrum. So what by Bragg's law look like a trivial condition that is $2D \sin \theta = n \lambda$ or $m \lambda$. Now it looks quite stringent because $\mathbf{k} - \mathbf{k}' = \mathbf{G}$. If you square this up and then we can write this $k'^2 = k^2 + G^2 - 2\mathbf{k} \cdot \mathbf{G}$.

Condition for constructive interference:

Or, $\vec{d} \cdot (\hat{n} - \hat{n}') = m\lambda, \quad m: \text{integer}$

Or, $\vec{d} \cdot (\vec{k} - \vec{k}') = 2\pi m,$ $\vec{d}: \text{arbitrary} = \vec{R}$

$(\vec{k} - \vec{k}') \cdot \vec{R} = 2\pi m,$ or, $e^{i(\vec{k} - \vec{k}') \cdot \vec{R}} = 1$

$(\vec{k} - \vec{k}') \text{ is a valid reciprocal lattice vector } = \vec{G}$

$\vec{G} = n_1 \vec{b}_1 + n_2 \vec{b}_2 + n_3 \vec{b}_3$

$e^{i\vec{G} \cdot \vec{R}} = 2\pi m$

$\vec{a}_i \cdot \vec{b}_j = 2\pi \delta_{ij}$

Thus, it puts a very stringent condition that for a constructive interference to occur the change in wavevector $(\vec{k} - \vec{k}')$ has to match a proper reciprocal lattice vector for a given lattice.

By Bragg's law, it looked like a trivial condition, now it looks quite stringent.

$(\vec{k} - \vec{k}') = \vec{G} \rightarrow k'^2 = k^2 + G^2 - 2\vec{k} \cdot \vec{G} \Rightarrow G^2 = 2\vec{k} \cdot \vec{G}$

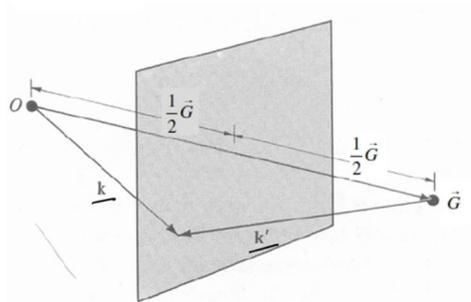
$k' \approx k^2$

Now, we know that K prime square equal to K square because of λ being same, that is the elastic scattering. Then we have this condition that comes out, which is G square equal to $2\vec{k} \cdot \vec{G}$. So, that is actually the Von Laue formalism that it says, okay. So, if we, you know, putting it in another form is that the half of the reciprocal lattice vector, which is G over 2, is it should be such that the K is in the direction of the G or the projection of K in the direction of G has to match exactly with half the reciprocal lattice vector. Geometrically one can really think of this as so you have a K coming here.

and you have a K prime and it is falling on a crystal plane and say there is a G that is connecting from the origin to this point there. So, the crystal plane must lie at the perpendicular bisector there. So, it must lie at the middle point for the scattering to give rise to constructive interference. This is what is written the component of the incident wave vector along the reciprocal lattice vector must be half of the length of G . So, an incident X-ray will satisfy the one lower condition if the tip of K lies in a plane that is perpendicular to the bisector. So, that is a perpendicular bisector of a line joining the origin and a reciprocal lattice point.

Equivalently,

$$\frac{G}{2} = \vec{k} \cdot \frac{\vec{G}}{G}$$



The component of the incident wavevector \vec{k} along the reciprocal lattice Vector must be half the length of \vec{G} .

An incident X-ray will satisfy Laue condition if the tip of \vec{k} lies in a plane That is perpendicular bisector of a line joining the origin and a reciprocal lattice point.

So, what was looking like a very simple condition in Bragg's law, now it looks like that the incident X-ray and the scattered X-ray, their wave vectors have a very intimate relationship with the reciprocal lattice vector of a particular lattice. So, that is why the Bragg diffraction is specific to a given crystal. So, the planes that you see for a simple

cubic, you will not be able to see that same plane say for a HCP structure. Or for another diamond structure. And that's the power of this method that every crystal structure presents you with an output which helps you to determine the exact crystal structure position of the atoms or the ions and which planes are involved and so on and so forth.

So, but at the end of the day, there has to be an equivalence between Bragg's law and the Von Law formalism. Okay. So, we have seen this that for elastic scattering K equal to K prime. So, the shortest reciprocal vector connecting different planes in the reciprocal space is G_0 equal to 2π over d . So, the reciprocal lattice vector that we talk about here or in the last slide, there must be some integer times the smallest reciprocal lattice vector.

So, this is $N g_0$, so g equal to $N g_0$, which has to be equal to 2π by D into N , where D is the spacing between the different planes. So, from the figure if you see that these are k 's direction of k and that is k prime here and k has a direction which is in this direction but so this is taken as a minus k direction the one that is up there and then this is the g vector which is equal to k minus k prime or k prime minus k . So, it is basically k prime so g is equal to k prime. plus minus of k and this is equal to k prime minus k . So, that is the condition that we have. Now from this figure, you can easily see that G is equal to $2K$ sine theta because this K is a scalar quantity where K is equal to K prime and if you put in G to be equal to 2π by D into N , you get a $2D$ sine theta equal to N lambda which is what you have learnt in Bragg's law. So, the Von Loewe formalism, even though it looks quite stringent and quite sophisticated as well because it does not make a lot of assumptions which Bragg's law did, eventually it gives rise to the same result which it should, whether you take one formalism or the other, the physical results do not change.

Equivalence of Bragg's law and von Laue Formalism

For elastic scattering, $|\vec{k}| = |\vec{k}'|$.

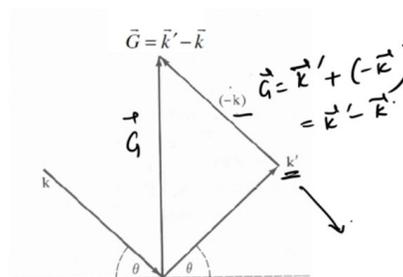
Also the shortest reciprocal vector must connect successive planes.

$$|\vec{G}_0| = \frac{2\pi}{d}$$

Also, $\vec{G} = n\vec{G}_0 \Rightarrow |\vec{G}| = n|\vec{G}_0| = \frac{2\pi}{d}n$

From the figure, $|\vec{G}| = 2k\sin\theta$

Hence, $2d\sin\theta = n\lambda$ Bragg's law.



Now, we come to this intensity of the Bragg peaks and we talk about the structure factor, we talk about the selection rules and whether all planes will be there for a given crystal structure or there are certain planes that are missing and how do we a priori know that which peaks we would not see for a given crystal structure. Say, for example, for FCC, are we going to see all peaks as we have seen it for simple cubic? If that is true, then there is no way of determining that which one is simple cubic and which one is FCC. So there has to be certain other condition that should come in. And here, as we have said earlier, that there is a diffraction intensity also forms a role.

Basically, the y-axis or the height of a peak and so on. And so, as I said, that a simple cubic lattice should be distinct from HCP lattice or from a zinc blend structure and so on. So, suppose there is a black peak that is associated with a change in wave vector G . which is Bragg's condition or the Von Laue condition. The path difference between the rays scattered at two locations d_i and d_j , where d_i and d_j are the locations of two atoms in the crystal lattice, then the path difference is $G \cdot d_i - d_j$.

Intensity of the Bragg peaks: Structure Factor, Selection rules

1. The crystal structure should play a role on the diffraction intensity.
2. An SC lattice should give distinct pattern compared to the HCP lattice.
3. If a Bragg peak is associated with a change in wavevector \vec{G} , the path difference between the rays scattered at \vec{d}_i and \vec{d}_j is $\vec{G} \cdot (\vec{d}_i - \vec{d}_j)$.
4. Phase difference is $e^{i\vec{G} \cdot (\vec{d}_i - \vec{d}_j)}$.
5. Therefore, the phases of different rays scattered from $\vec{d}_1, \vec{d}_2, \dots$ are in the ratios $e^{i\vec{G} \cdot \vec{d}_1}, e^{i\vec{G} \cdot \vec{d}_2}, \dots$ etc
6. A scattered X-ray will pick up all these phases, $S_{\vec{G}} = \sum_{j=1}^n e^{i\vec{G} \cdot \vec{d}_j}$. $S_{\vec{G}}$ is called as the geometric structure factor.
7. The intensity of the Bragg peak will be proportional to $|S_{\vec{G}}|^2$

So, if this is the path difference, the phase difference is given by exponential $i g \cdot d_i - d_j$. So, that is the phase difference, and this phase difference we know that it has to match certain multiples of lambda. So, if you have all these crystal lattice or lattice points that are placed at d_1, d_2, d_3 from some chosen origin where d_1 is a vector that connects the first atom, d_2 is the second atom and d_3 is the second. Third atom and so on.

So, then they have these the phases of the scattered rays will R will be in the ratios of these phases, which are exponential $i \mathbf{g} \cdot \mathbf{d}_1$ and $i \mathbf{g} \cdot \mathbf{d}_2$ and so on and so forth. So, a scattered X-ray will pick up all these phases, and we will get what is called a geometric structure factor, which will be expressed in terms of the sum of all these phases that would come, okay.

So, the intensity of the Bragg peak would be proportional to this SG mod square and that will be the height of the output spectrum in a X-ray diffraction experiment, okay. Now the total scattering amplitude would be proportional to these sum over or integration of $dV n_r \exp(i \mathbf{k} \cdot \mathbf{r} - \mathbf{k}' \cdot \mathbf{r})$. Once again \mathbf{k} and \mathbf{k}' are these incident and scattered X-ray wave vectors. n is basically an electronic concentration that lies within a small volume dV . And $\mathbf{k} - \mathbf{k}' = \Delta \mathbf{k}$, which has to be equal to \mathbf{g} , the proper reciprocal lattice vector. So, if you put that there, so your $\Delta \mathbf{k} = \mathbf{g}$ is put in this, so this is equal to \mathbf{g} , and we have $n_r \exp(-i \mathbf{g} \cdot \mathbf{r})$.

Now, because of the crystal structure, we have these densities of the electron densities would be repeating in a periodic fashion. So, as you go from some point R with respect to some chosen origin, you go to $R + \mathbf{R}$, where \mathbf{R} is the direct lattice vector. You see the same density there. So, this we can write it that we, you know, integrate over all the cells, and then there is a sum over R , and it is $n_R \exp(i \mathbf{g} \cdot \mathbf{R})$, which is equal to, you know, which is $n \exp(i \mathbf{g} \cdot \mathbf{R})$, and it is exponential minus $\mathbf{g} \cdot \mathbf{R}$, which is equal to, you know, so the n , we do these, there are n of the, this direct lattice vector. So, this sum over R is now replaced by this n .

So, we have these total scattering amplitude which is f of \mathbf{g} which is equal to n into integral over some unit cell into $dV n_r \exp(-i \mathbf{g} \cdot \mathbf{r})$. So, that is exactly what we write once again, and that is nothing but NSG , where SG is what we have defined in the last slide. So, SG is called the geometric structure factor, and we will have to eventually find the intensity of the Bragg peak, which is proportional to SG squared. So, Sg is nothing but this sum over j of $N_j \exp(-i \mathbf{g} \cdot (\mathbf{R} - \mathbf{R}_j))$ and this exponential minus $\mathbf{g} \cdot \mathbf{R}$, and we write that in terms of, say, $\mathbf{R} - \mathbf{R}_j$ as some vector called $\boldsymbol{\rho}$, and we take this minus $\mathbf{g} \cdot \mathbf{R}_j$ outside, and then the integral is $dV \sum_j \exp(-i \mathbf{g} \cdot \boldsymbol{\rho})$ where $\boldsymbol{\rho}$ is nothing but $\mathbf{R} - \mathbf{R}_j$. \mathbf{R} is a general lattice point that is any arbitrary lattice point with respect to some origin is written as \mathbf{R} and \mathbf{R}_j is the individual lattice points.

Further, the total scattering amplitude is defined as:

$$F = \int dV n(\vec{r}) e^{i(\vec{k} - \vec{k}') \cdot \vec{r}} = \int dV n(\vec{r}) e^{-i\Delta\vec{k} \cdot \vec{r}}$$

With $(\vec{k} - \vec{k}') = \Delta\vec{k} = \vec{G}$ and $n(\vec{r})$ is electron concentration within dV .

$$F_{\vec{G}} = \int dV n(\vec{r}) e^{-i\vec{G} \cdot \vec{r}} = \sum_R \int_{\text{cell}} dV n(\vec{r} + \vec{R}) e^{-i\vec{G} \cdot (\vec{r} + \vec{R})} = \sum_R \int_{\text{cell}} dV n(\vec{r}) e^{-i\vec{G} \cdot \vec{r}} = N \int_{\text{cell}} dV n(\vec{r}) e^{-i\vec{G} \cdot \vec{r}}$$

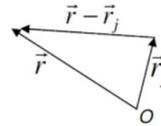
$$F_{\vec{G}} = N \int_{\text{cell}} dV n(\vec{r}) e^{-i\vec{G} \cdot \vec{r}} = N S_{\vec{G}}$$

$n(\vec{r}) = \sum_{j=1}^s n_j(\vec{r} - \vec{r}_j)$ It is convenient to write the total electron density $n(\vec{r})$ as various n_j associated with j^{th} atom.

$$S_{\vec{G}} = \sum_j \int dV n_j(\vec{r} - \vec{r}_j) e^{-i\vec{G} \cdot \vec{r}}$$

$$= \sum_j e^{-i\vec{G} \cdot \vec{r}_j} \int dV n_j(\vec{\rho}) e^{-i\vec{G} \cdot \vec{\rho}}$$

$$\vec{\rho} = \vec{r} - \vec{r}_j$$



So, rho is equal to R minus Rj. So, this helps us define the atomic form factor, which is defined as this dV Nj rho exponential minus iG dot rho. So, Sj becomes equal to this Fg here and the sum over j of exponential minus G dot rj. And G is, of course, different for different lattice geometries. So, Sj becomes equal to Fj into exponential minus 2 pi i p x j q y j and z r j and then there is a sum over j.

So, if you have, say, 2 atoms per unit cell, you will have to sum over 2 terms, where Xj, Yj, and Zj are the coordinates of those 2 atoms with respect to some origin. Usually, we choose the origin somewhere, say, at the corner of the lattice or at the middle of the lattice, and so on. So, p, q, r are, of course, integers, and they are nothing but the Miller indices, in fact. So, xj, yj, and zj are the coordinates of each of those points. And once we know that, let us formulate the selection rules for the FCC and the BCC structures. And we have that BCC has two atoms.

This helps in defining the atomic form factor:

$$f_j = \int dV n_j(\vec{\rho}) e^{-i\vec{G}\cdot\vec{\rho}}$$

$$S_{\vec{G}} = \sum_j f_j e^{-i\vec{G}\cdot\vec{r}_j}$$

Since, \vec{G} is different for different lattice geometry,

$$S_{\vec{G}}(p, q, r) = \sum_j f_j \exp[-2\pi i(px_j + qy_j + rz_j)]$$

(p, q, r) are the Miller indices (h, k, l)

They are located at the origin and at the body-centered place. So, if we put these two values for 0 0 0, we get 1, and for half of half, we get this factor. Now, you see that this is an exponential minus I pi h plus k plus l, where h plus k plus l is an integer. If it becomes an odd integer, then this one will cancel and will get a 0, the structure factor equal to 0, which means that there will not be any scattering peak or there will be no peak in the spectrum. Because S is equal to 0 and that will happen when H plus K plus L equal to an odd integer okay so for some values of so it cannot be like 1, 2 and 1 again so or 1, 2, 2 and so on.

So, 1 plus 2 plus 2 will become 5, which is an odd integer, so you will not have any scattering occurring there. So, 1, 2, 2 plane will not give you any scattering, whereas 1, 2, 1 plane or 1, 1, 0 plane will give rise to a scattering because 8 plus K plus L equal to even and then it will give a sort of scattering, which is equal to 2F. Similarly, if we talk about an FCC lattice which has 4 atoms which are 1 at the origin and there are 4 at you know the these there are 3 more at these locations or these coordinates which are 0, half, half, half, 0, half and half, half, 0. And if we put that there, we get a 1 for the 0, 0, 0 and then each one of them will give rise to 1, you know, term. So, that tells that you will have for h, k, l to be all even or all odd.

Selection rules for BCC and FCC

BCC \Rightarrow 2 atoms at $(0,0,0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$

$$\begin{aligned} S(h, k, l) &= f[1 + \exp\{-i\pi(h + k + l)\}] \\ &= 0 \text{ for } h + k + l = \text{odd integer} \\ &= \underline{2f} \text{ for } h + k + l = \text{even integer} \end{aligned}$$

FCC \Rightarrow 4 atoms at $(0,0,0)$, $(0, \frac{1}{2}, \frac{1}{2})$, $(\frac{1}{2}, 0, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, 0)$

$$S(h, k, l) = f[1 + \exp\{-i\pi(h + k) - i\pi(h + l) - i\pi(l + k)\}]$$

If (h, k, l) all even or all odd, $S = 4f$

If two are even and one odd or one even, two odd, $S = 0$.

For example, if it is 2, 2, 0 or 1, 1, 1, then we get a scattering intensity which is equal to 4F. So, if 2 are even and 1 is odd or 1 even 2 odd we get the scattering to be 0 because these would cancel with 1 and will not get any scattering. So, that is the selection rule and that is what says that it tells you about the magnitude of the intensity which is there in the y axis. And at least the proportionality will tell you and it will tell you that which all planes are capable of scattering X-rays. And then one assigns these HKL indices with respect to the planes and can figure out what the crystal structure is.

And then that sort of settles the issue that all these crystal structures that we have talked about, are you know obtained by this X-ray diffraction. So, we will stop here and we will start with something new next class.