An Introduction to Materials: Nature and Properties (Part 1: Structure of Materials)

Prof. Ashish Garg
Department of Material Science and Engineering
Indian Institute of Technology, Kanpur

Lecture - 36
X-ray Diffraction (contd.)

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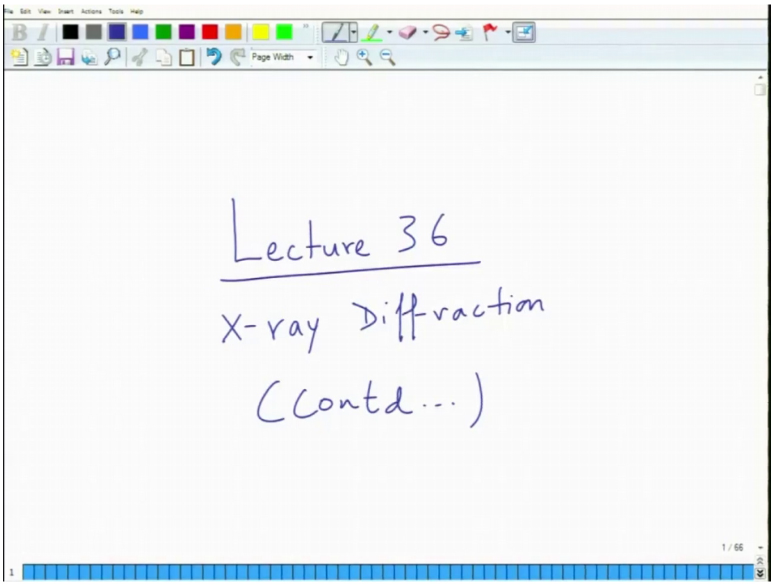

Lecture 36

X-ray Diffraction

(Contd...)

So, again we get back to the next lecture. As usual we will continue with X-ray diffraction. In this case, we will take example, one exercise of how to examine the crystal structure of a material, ok. So, what we have here is, what we will do is that first we look at the fundamentals of how do you, why do different, what why do different structures diffract differently, ok. Here I have not told you.

So far, I have only told you that for diffraction to occur u n lambda equal to d sin theta has to be obeyed, but it turns out when the diffraction goes through, when the X-ray beam enters the material, the planes which diffract the position of atoms, those planes determine which planes will diffract and which planes will not diffract because the position of atoms will determine the phase difference and the phase difference will affect whether there is a constructive interference, whether there is a destructive interference from.

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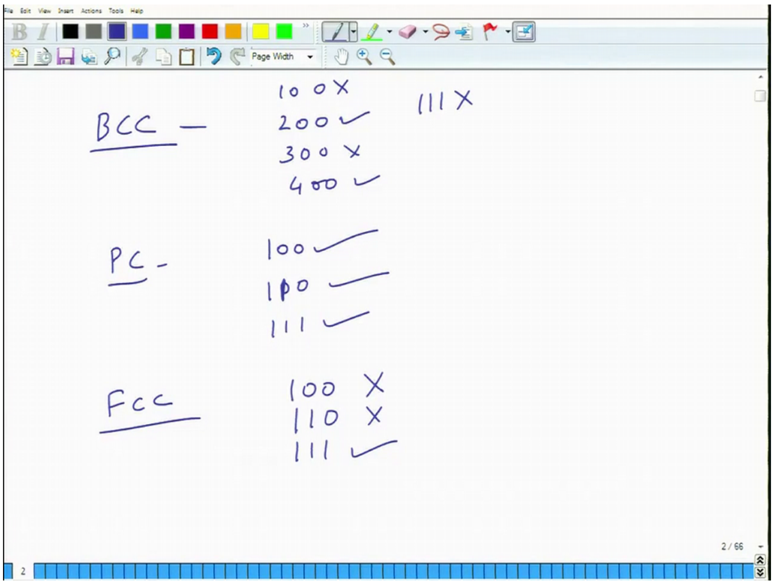

BCC — 100 ✗ 111 ✗
200 ✓
300 ✗
400 ✓

PC - 100 ✓
110 ✓
111 ✓

FCC 100 ✗
110 ✗
111 ✓

So, for example in case of BCC material as we will see 200 will diffract, but 100 will not diffract, 300 will not diffract, 400 will diffract. This is because of position of atoms, because BCC has an atom sitting at the center of the unit cell for a primitive cubic as we will see 10, all of the print planes diffract 100, diffract 110, diffracts 111, diffracts all of them. Diffract in this case 111 does not diffract for FCC. We will see where we have atom sitting at the center of the faces, we will see that 100 does not diffract, 110 does not diffract, but 111 diffracts and so on and so forth.

So, we will find first what is the condition for diffraction from various crystals and then, we will examine X-ray diffraction pattern to find out the type of the crystal.

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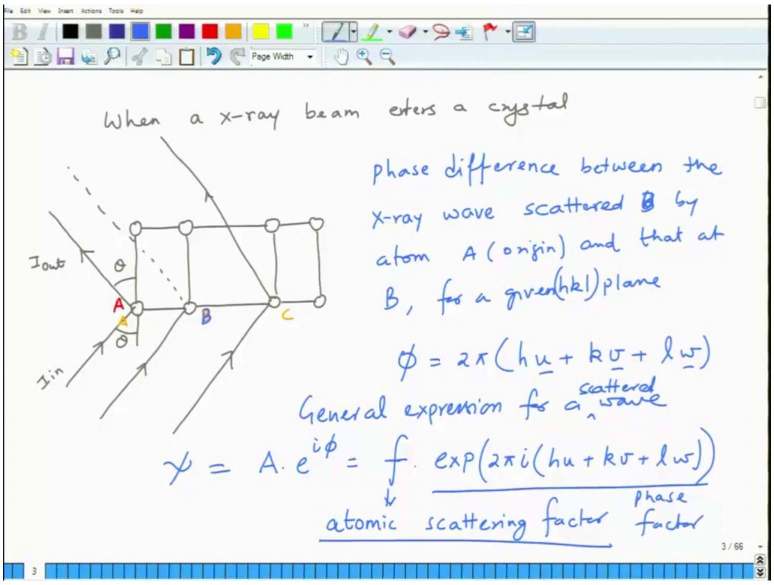

When a x-ray beam enters a crystal

phase difference between the X-ray wave scattered B by atom A (origin) and that at B, for a given (hkl) plane

$$\phi = 2\pi(h\underline{u} + k\underline{v} + l\underline{w})$$

General expression for a scattered wave

$$\psi = A\cdot e^{i\phi} = \underbrace{f}_{\text{atomic scattering factor}}\cdot\underbrace{\exp(2\pi i(hu + kv + lw))}_{\text{phase factor}}$$

So, when the diffraction occurs through crystals, so let me draw a geometry here and let us say, so the when enters a crystal, it undergoes diffraction, ok. So, there are two. So, they could be let us say various atoms. So, we have an atom A here. So, let me draw our drawing here. So, we have an atom sitting here let us say and then, we have another atom sitting here, ok.

Let us say this atom is A, this is B, this is C and so, these are few atoms and let me now draw the, I am not going all the planes here, but it is just that I have. So, you can have one sitting here, and let us say we have an incoming beam 1. Let us say this is I in this is A atom, ok. A has been rubbed out and this is the diffracted beam which is I out. Similarly, you will have one for B and there will be one from the diffracted beam from one. So, this is and then of course, you will have one from here and then here.

So, I have not drawn the atoms. In between you will have successive atoms, all over the place and let us say the distance, this angle which is here is theta and this is also theta. So, the phase difference between, so now I write the phase difference between the X-ray wave scattered by because atoms will scatter, right. So, scattered by B, atom B which is sitting here, this is B, and that scattered by.

So, if this is the origin A scattered by B by atom, sorry atom A at origin and that at B which is another position, for a given hkl reflection for a given hkl plane, this phase difference is 2 pi h u plus kv plus lw. We are uvw are the coordinates of the atoms and you can see that this phase difference is only dependent upon the position uvw. Uvw are the coordinates, hkl are the plane indices. There is nothing about size and shape, there is nothing about the length, there is nothing about the inter planar angles and so on and so forth.

So, if you have az, if you want to write a general expression for a general expression for a wave which is scattered for a scattered wave, you can write this as A into I. So, basically wave equation a into i phi which is related to a factor called as f exponential of 2 pi i into hu plus l w, where f is a factor which is called as atomic scattering factor.

Basically, this is the wave equation which tells you that f will determine the amplitude. How much the wave is scattered will be determined by a type of atom where it is a heavy atom, where it is a light atom whether it is a medium atomic weight atom. So, this will determine the amplitude and this will determine the phase difference. This is the phase term, this is the amplitude term which is for a given phase equation, right.

So, this is nothing, but psi, ok. Psi is the wave equation which is equal to A exponential I phi, where A is the amplitude and exponential I phi is the phase term amplitude. It is determined by the capability of atoms to scatter the wave. How much they will scatter which is dependent upon number of electrons and so on and so forth. They have so, this is atomic scattering factor and this is the phase factor ok.

So, if phase factor turns out to be 0, you will have no diffraction at all. If phase factor turns out to be finite, you will have some diffraction taking place.

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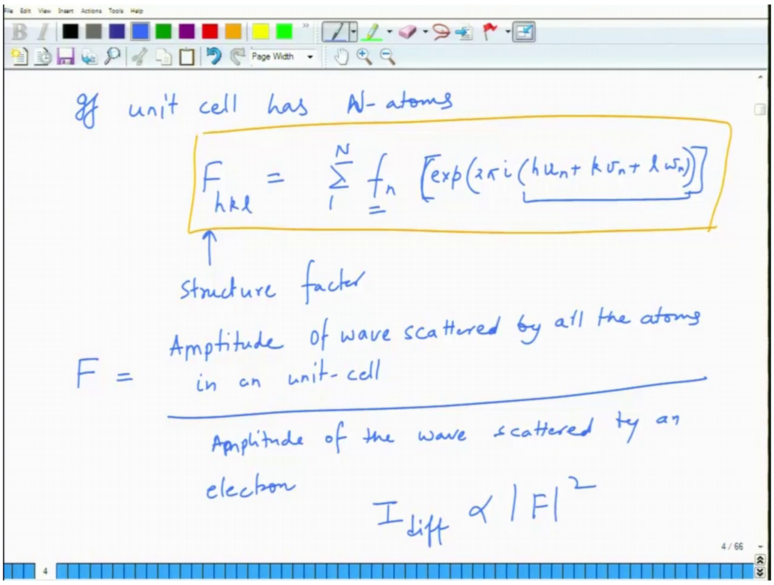

If unit cell has N- atoms

$$\boxed{F_{hkl} = \sum_{1}^{N} \underline{\underline{f_n}} \left[\exp\left(2\pi i \left(\underline{hu_n + kv_n + lw_n}\right)\right)\right]}$$

↑

Structure factor

$$F = \frac{\text{Amptitude of wave scattered by all the atoms in an unit-cell}}{\text{Amplitude of the wave scattered by an electron}}$$

$$I_{diff} \propto |F|^2$$

So, if the unit cell consists of n number of atoms, if unit cell has n atoms, then I can write I can define a term capital F hkl which is sigma over 1 to n f n into exponential of 2 pi i h u n plus kv n plus l w n and interestingly for a given crystal, we do not have to go for too many uvws because crystal is periodic. So, we do not need to consider all the millions and zillions of atoms.

You just need to since crystal is periodic; you are confined to the atoms which are within the unit cell only because the rest of them are going to behave in the same manner, alright. So, we do not have to take too many uvws. We just have to take those uvws of those atoms which are present within one unit cell because all others are going to behave in the same fashion. So, this F is called as structure factor and this small f is atomic scattering factor.

So, what this equation tells you is that depending upon the type of atom, you will have different scattering that are going to take place and you have a phase term which is dependent by which is determined by the position of atoms. There is nothing about size and shape here. So, if you have different types of atoms, for example in the unit cell, they will diffract differently. So, for example, copper zinc. Copper will have different small f, zinc will have different small f, but if you have only copper, they will have same small f.

So, this will have strong bearing on the. So, basically I can define f as basically amplitude of the physical definition is amplitude of wave that is scattered by all the atoms in an unit cell divided by amplitude of the wave scattered by one electron, an electron. So, this is the physical definition. The structure factor is amplitude of the wave is scattered by all the atoms in an unit cell divided by amplitude of the wave is scattered by single electron.

So, this F hkl, the equation that I have written here, this is the one and this F hkl, so amplitude intensity of beam. So, I diffracted beam is proportional to mod of f square, ok. So, if f is finite, your i is finite. If i diff is 0, your i is 0.

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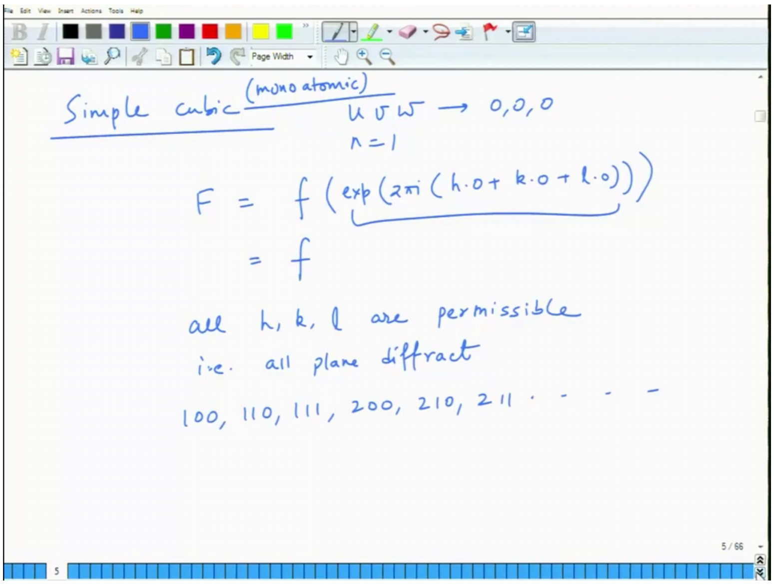

Simple cubic (mono atomic)

$u\,v\,w \rightarrow 0,0,0$

$n = 1$

$$F = f\left(\exp\left(\underline{2\pi i\left(h\cdot 0 + k\cdot 0 + l\cdot 0\right)}\right)\right)$$

$$= f$$

all h, k, l are permissible

i.e. all plane diffract

100, 110, 111, 200, 210, 211 . . . . –

So, we will see now in the case for let us say BCC is simple cubic structure first of all, so, let us say simple cubic. So, simple cubic what is uvw? You have only one atom which is at 000 and your small n is equal to 1. So, capital F is equal to small f multiplied by simple unit you can say mono atomic, small f into exponential of 2 pi i h 0 plus plus l 0.

So, you cannot get any condition here which means this factor is equal to 1. So, F is equal to f which means there is no dependence of hkl on the position of atom. As a result you can say all hkl are permissible. So, independent of hkl all you will see all the hkl's will diffract, all the planes will diffract, which means that is all planes diffract. So, 110 111 200 210 211 and so on and so forth all will diffract.

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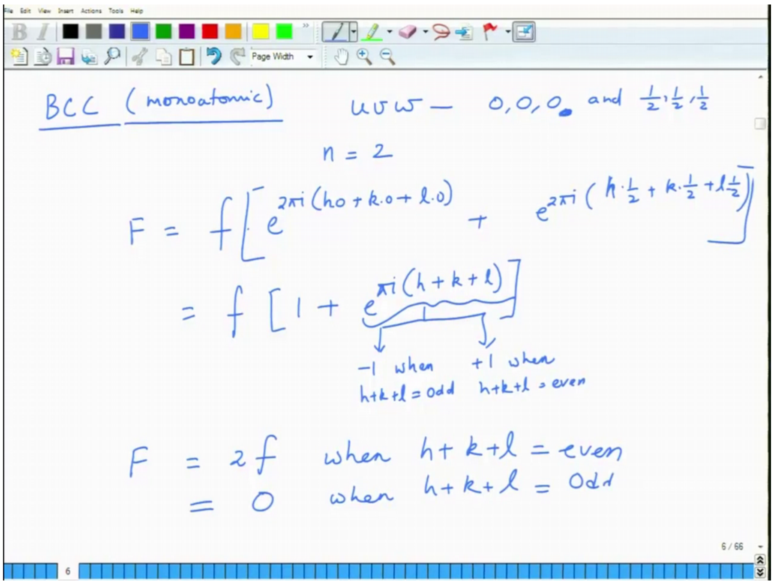

BCC (monoatomic) uvw — 0,0,0 and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$

$n = 2$

$$F = f\left[e^{2\pi i(h0 + k.0 + l.0)} + e^{2\pi i\left(h.\frac{1}{2} + k.\frac{1}{2} + l\frac{1}{2}\right)}\right]$$

$$= f\left[1 + \underbrace{e^{\pi i(h+k+l)}}_{\substack{-1 \text{ when } h+k+l = \text{odd} \qquad +1 \text{ when } h+k+l = \text{even}}}\right]$$

$$F = 2f \text{ when } h+k+l = \text{even}$$
$$= 0 \text{ when } h+k+l = \text{Odd}$$

Now, let us see if you go to BCC, again monoatomic only one type of atom. Now, what is uvw for BCC, 000 and half half half number of atoms is 2. If it is same type of atom, then I can write this capital F to be equal to since it is, so f into first term 2 pi i h 0 plus plus l 0 plus again small f 2 pi i h into half plus k into half plus l into half. So, this will become, so you can say you can take this out and this f will go from here, ok.

What is this term? This is 1, this is e to the power pi i h plus k plus l when is this term finite. So, h plus, so you can see that this will become minus 1 when h plus k plus l is odd. This whole term and this will become plus 1 when h plus k plus l is even because e to power i theta is equal to sin theta cos theta plus plus i sin theta, ok. So, when this is minus 1, then this is cos of. So, when this is odd, so let us say just 1, ok. So, this will become cos pi plus i sin pi sin pi is 0 cos pi is minus 1. So, this will become minus 1.

Similarly, cos 3 pi cos 4 pi cos 5 pi and so on; When it is even, then it will be plus 1, all right. So, as a result now what you get condition for this capital F is equal to 2 f when h plus k plus l is even is equal to 0. When h plus k plus l is odd, what does it mean?

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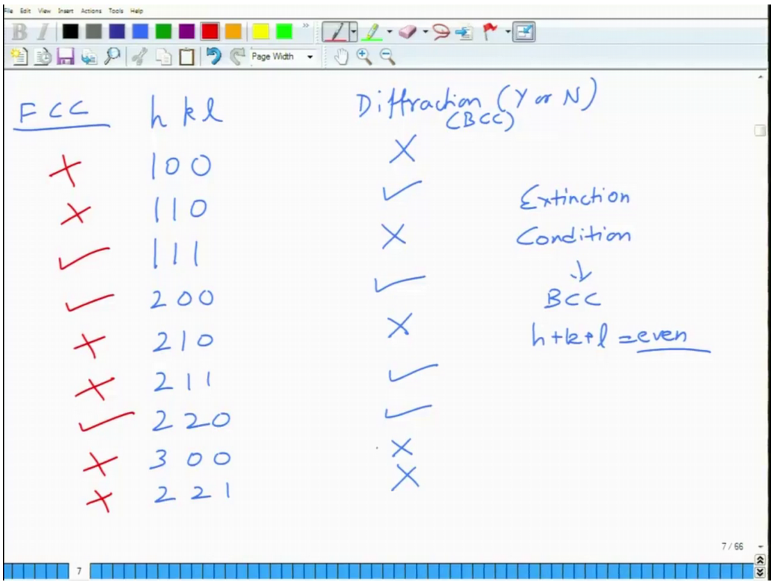

FCC	hkl	Diffraction (Y or N) (BCC)
✗	100	✗
✗	110	✓
✓	111	✗
✓	200	✓
✗	210	✗
✗	211	✓
✓	220	✓
✗	300	✗
✗	221	✗

Extinction Condition
↓
BCC
$h+k+l = \underline{\text{even}}$

So, now if I write a series of hkl and diffraction yes or no I start from 100. Well, it diffract 110 will diffract 111. It will not diffract 200, it will diffract 210. It will not diffract 211, it will diffract similarly now. So, this is what is the next one. It will diffract what else? 300. It will diffract 221 so on and so forth. You keep building this series, ok.

So, for BCC the condition is only those planes will diffract for which h plus k plus l is even and this basically means that 1100, those planes which do not diffract for them, the interference is destructive in nature because the presence of an atom in the central atom within the unit cell.

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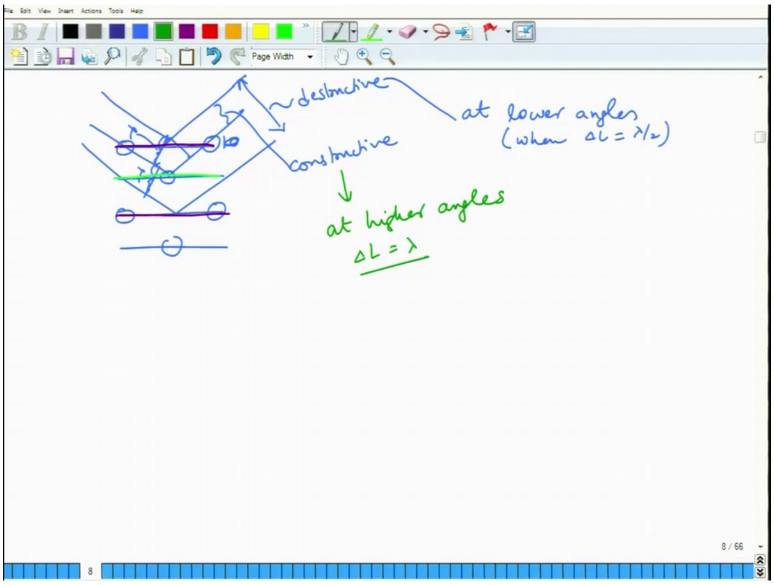

So, if I draw this, so you have this. This is let us say you have two atoms here, one atom here, you have two atoms here and then, one atom here. So, it turns out when the incoming wave comes like this. So, every 200 will diffract. So, what will happen is between successive, the path difference is it leads to destructive interference, but if you take these, then these lead to constructive interference.

So, basically the wave which is scattered from the middle plane is out of phase with the wave which is scattered from the top and bottom plane. So, basically you can say that you will have this will be lambda by 2. So, they will cancel each other. As a result you will not have any 100, but if you go to higher angles from the change, angle changes, then between these two you will have lambda, ok.

So, at smaller angle the path difference is such that, so that when you look at first order 100, then the path difference lambda by 2 and lambda by 2, they all cancel each other; Nothing different. When you go to higher angle, then this path difference becomes lambda and this also becomes lambda, all right. So, this is at lower angles when path difference is delta l is lambda by 2 between the successive planes and successive planes are these.

So, this is first plane, this is second plane, these are successive planes and then, when you go to higher angles at higher angles, the delta l becomes lambda, then the diffraction occurs. So, 220 peak is nothing, but second order 100, right.

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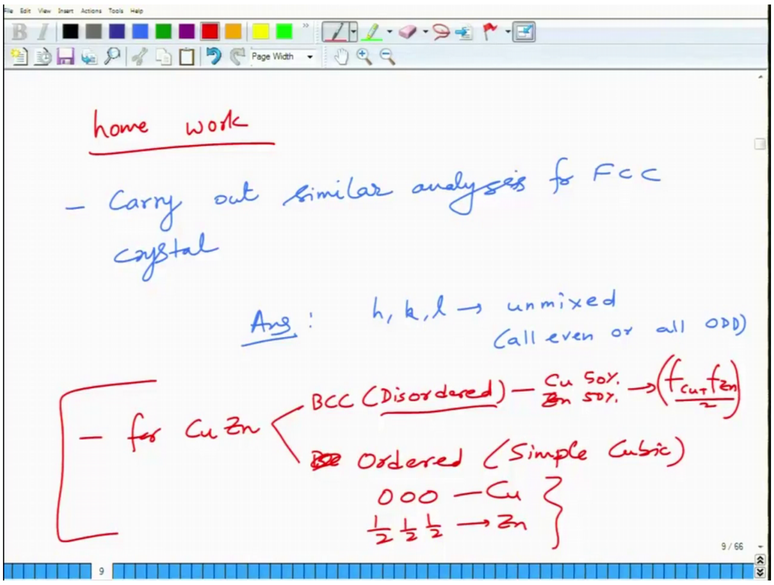

home work

- Carry out similar analysis for FCC crystal

Ans: h, k, l → unmixed (all even or all ODD)

- for Cu Zn

BCC (Disordered) — Cu 50%, Zn 50% → $\left(\frac{f_{Cu}+f_{Zn}}{2}\right)$

~~BC~~ Ordered (Simple Cubic)

000 — Cu

$\frac{1}{2}\frac{1}{2}\frac{1}{2}$ → Zn

So, position of atom makes a difference there. So, similarly if you do the same analysis for FCC, I will leave you as a home exercise, homework. These are called as basically extinction conditions, ok. So, for BCC it is h plus k plus l should be even for diffraction to occur. So, as a homework you can say carry out similar analysis for FCC crystals. So, for FCC crystal you will answer I will give you the answer. The answer is hkl should be unmixed. That is all even or all odd.

So, if I go to previous slide now again, so this is for BCC, ok. If I do the same for FCC, then you can see that this is mixed zero is considered as even. So, this will not diffract, this will not diffract, this will diffract, this will diffract, this will not diffract, this will not diffract, this will diffract, this will not diffract this one. So, you can see that far lower number of peaks diffract in case of FCC.

You can see in case of simple cubic, everything diffracts and BCC every alternating peak is diffracting. In case of FCC, very few peaks diffract. So, you can see if you give an x-ray diffraction pattern of a given material just by looking at it, you might be possible to just guess what material is it. If it is a single phase material, of course, so let me now and same analysis you can also do for let us say for Cu Zn Cu Zn in BCC form which is disordered form.

So, you consider there as two atoms Cu Cu at 50 percent cu and 50 percent Zn. So, F will be f Cu plus f Zn divided by 2 for BCC or for ordered crystal, it is simple cubic and here you have one atom at 000 which is copper and another atom at half half half is zinc.

So, you will see that order disordered the transformation in crystals can be seen only through X-ray diffraction very easily because one will show you X-ray diffraction pattern which is like BCC and the one will show you X-ray diffraction pattern which is like simple cubic, ok. So, the extra peak which will come out in simple cubic, they will be called super lattice reflections. So, we will not get into details of them, but let me now just summarize the part.

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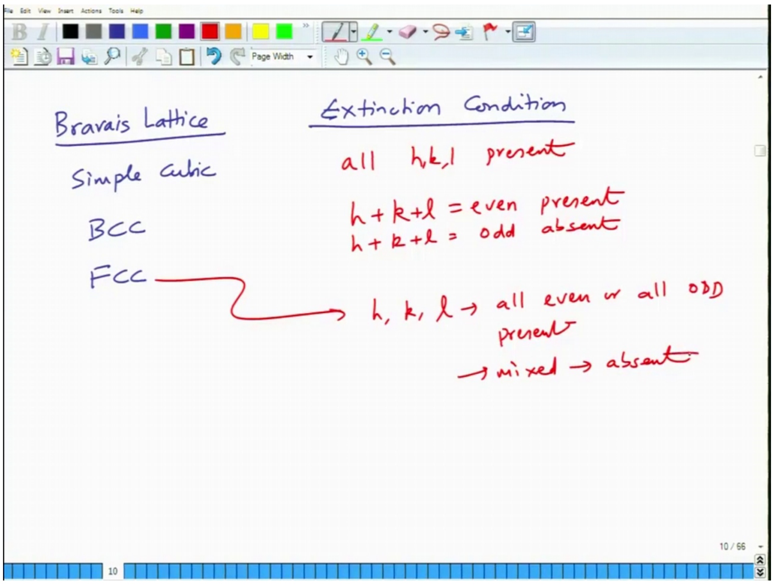

Bravais Lattice	Extinction Condition
Simple cubic	all h,k,l present
BCC	$h+k+l$ = even present $h+k+l$ = odd absent
FCC	h, k, l → all even or all ODD present → mixed → absent

So, with respect to Bravais Lattice if you have simple cubic, if you have BCC and you have FCC ok, there are other lattices for which you can do yourself, reflections which are extinction condition.

So, you can write here all hkl present, ok. Basically all peaks diffract here. Only h plus k plus l is equal to even present and h plus k plus l odd absent and in this case, hkl all even or all odd present and mixed absent.

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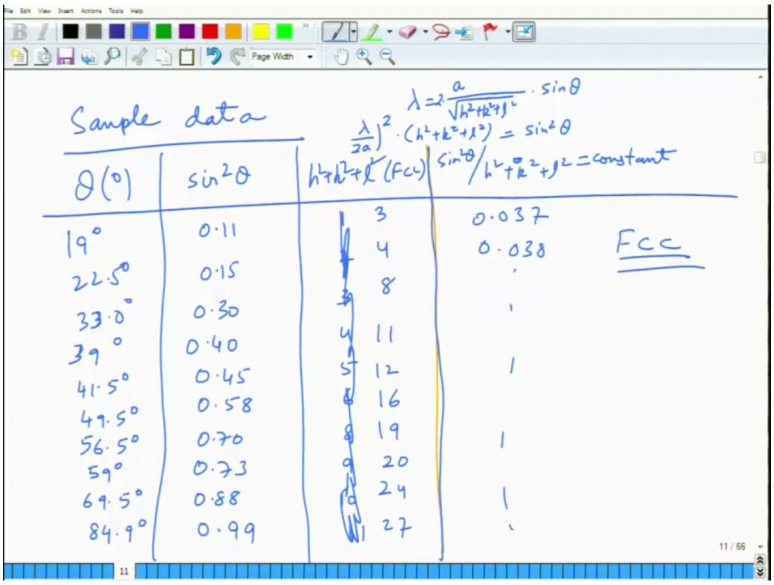

Sample data

$$\lambda = 2\cdot\frac{a}{\sqrt{h^2+k^2+l^2}}\cdot\sin\theta$$

$$\left(\frac{\lambda}{2a}\right)^2\cdot(h^2+k^2+l^2) = \sin^2\theta$$

θ (°)	$\sin^2\theta$	$h^2+k^2+l^2$ (Fcc)	$\sin^2\theta / h^2+k^2+l^2$ = constant
19°	0.11	3	0.037
22.5°	0.15	4	0.038
33.0°	0.30	8	
39°	0.40	11	
41.5°	0.45	12	
49.5°	0.58	16	
56.5°	0.70	19	
59°	0.73	20	
69.5°	0.88	24	
84.9°	0.99	27	

Fcc

Now, let us do a simple analysis for the crystal that we have examined. So, let me say just let us say the sample data is from the X-ray diffraction pattern. The sample data says your thetas occur at 19 degree, 22.5 degree, 33 degrees, 39 degrees, 41.5 degree 49.5 degree, 56.5 degree, 59 degrees, 69.5 degree and 84.9 degree.

These are the peaks that you observe in your X-ray diffraction pattern, ok. To do this is theta naught 2 theta 2 theta divided by 2 and we know that for a cubic crystal lambda is equal to a divided by 2 into a divided by root of h square plus a square plus i square into sin theta. This is the formula that we know.

So, lambda divided by 2 a is fixed square into h square plus k square plus l square. This is equal to sin square theta. This relation I know. Now, we need to identify the lattice parameter in crystal structure of the given material, ok. So, sin square theta is basically proportional to h square plus k square plus l square. So, let us do the sin square theta calculation. Sin square theta will work out to be 0.11 0.15 0.30 0.40 0.45 0.58 0.70 0.74 0.88 and 0.99.

So, if you want to now find out if you want to convert these into integers, all you need to convert these into integers and you need to convert these integers. So, let us say for you can, there are two ways of doing it. You can do it manually or you can divide it by the smaller number and then, convert it into integers. So, when you convert it to integers, you find out that it matches to what we call as. So, we can do it first manually for simple cubic case h square plus k square plus l square should be equal for simple cubic.

For that we know it is 1 2 3 4 5 6. There is no 7 8 9 10 11, all right which means my sin square theta divided by h square plus k square plus l square should be constant, right. If this is fine, let me work out 0.11 0.75 0.10 0.10 0.097 0.0925 0.081 0.088 and 0.09, ok. They are not equal. They are all different to each other. As a result it is not simple cubic. Now, let us examine for the case of h square plus k square plus l square for BCC.

So, if you examine for BCC, again you will see that it will not be equal. It is only when you examine it for FCC. For FCC the conditions are, so BCC you can do yourself. I will do it for FCC. So, if we examine theta divided by h square p scale square, so for FCC these are not the ones. For FCC, it would be 3 4 8 11 12 16 19 20 24 27 and if I now workout, if I now remove these, and I write the values, I will get 0.037 0.038 and so on and so forth. We will see that all the values will be equal.

So, this is basically FCC structured material. If all the values are same, then this is FCC structured material. So, once you know this ratio, we can find out if lambda is known. You can also find out what is a, right. So, individually you can find out a for different peaks and you can calculate what is the average a value, what is the standard deviation and so and so forth. So, this is a basic method to calculate the lattice parameter of any structure of materials.

So, this is bare minimum information about X-ray diffraction patterns which I have given you in past few lectures and in the next lecture, I will give you some more information as to what all like you can do with X-ray diffraction before we can move on to crystal defects, ok.

Thank you.