Techniques of Materials Characterization
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Lecture – 53
Intensity of diffracted beam (Continued)

Welcome everyone to this NPTEL online certification course on Techniques of Materials Characterization. So, we are on module 11 and we are discussing about X-ray diffraction. Until up to now, in this module we have developed the relationship or the equation for calculating the structure factor and we discussed about the importance of structure factor. Basically structure factor calculates, or structure factor relates the crystalline structure or crystal arrangement.

Atomic arrangement in a crystalline material to the X-ray diffraction that we finally receive the intensity of X-ray diffraction finally, we receive. And we see that a structure factor is basically very important because even if the Bragg's condition is satisfied for certain planes, due to the structure factor or due to the restrictions imposed by structure factor we do not get certain atomic planes even though the Bragg's angle, Bragg's condition is satisfied for them.

Certain planes we do not get any kind of intensity. So, this we have derived for until up to now, in the last class we derived it such relationship structure factor for 2 crystal systems. One is the simple cubic and another one is a base centered. One is the simple crystal structure or simple orthogonal crystal structure and one is the base centered orthogonal crystal structure.

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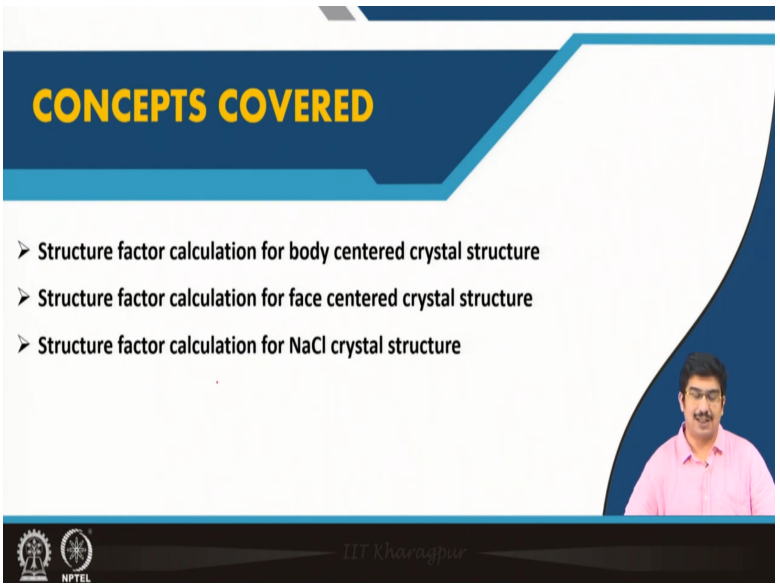

So now, in this week again we will be continuing this discussion and we will calculate the structure factor for 2 other types of 2 other general types of crystal structures, body centered. One is body centered crystal structure and other one is the face center crystal structure. And if time permits, we will try to do structure factor calculation for a more complex crystal structure that is a NaCl crystal structure.

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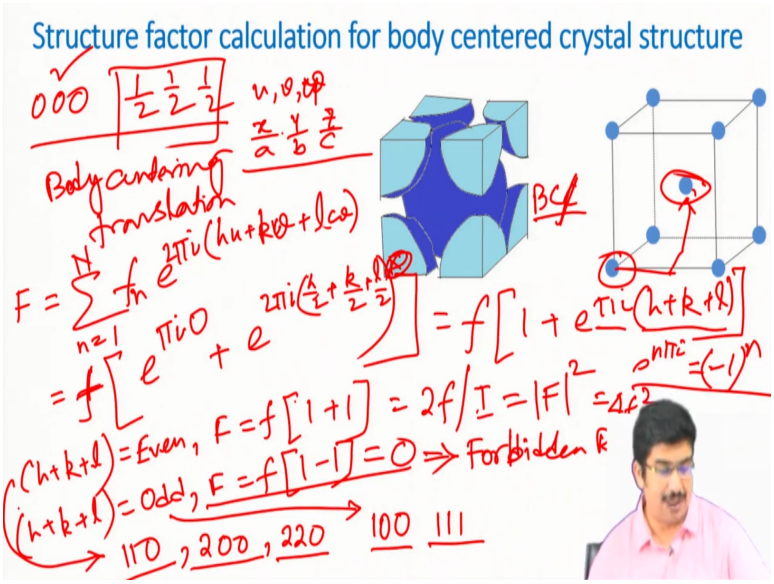

So, let us start this, our discussion on the structure factor calculation for a body centered crystal structure. So, here we have shown this is the BCC, body centered crystals. This is a body centered structure not a body centered cubic structure as such. We are it is a more of a generalized structure so, we will possibly omit this last C and we will call it a body centered crystal structure.

So, here we as we can understand it has 2 different type 2 atomic positions. One set of atom is obviously at the corner position and we by now, we know that this is one set of that atom, 0 0 0 is the position of that atom and then one another set of atom is this one which is lying somewhere within this crystal structure within this unit cell. And that is called the body centric position and that position we can write it in terms of the fractional relationship.

If you remember u v w which was basically u v w just for yourself, I am writing it again u v w which is nothing but basically x by a y by b and z by c the fractional coordinates. So, in the same way now, we are writing the fractional coordinates of that position as half, half, half. So, this is the body centering the 2 atomic positions for a body centered unit cell and this one, half, half, half this is called body centering translation.

This means basically that if you take a corner atom 0 0 0 and if you apply this translation over this 0 0 0 position corner atom this atom let us say, if we apply this half, half, half translation, this atom will go. So, if we start with this one we apply an half here, half here and half in z direction we arrive at this body centering position. So, half, half, half is basically called the body centering translation.

So now, we know the structure factor how it should be returned. So, structure factor is basically where n = 1 to capital N f n e phi i into basically e 2 phi into h u + k v + l w. So, this is the general formula for structure factor calculation. So, we are now, applying this on a body centered crystal. So, what we can write the first one and let us assume that this is composed of the same type of crystal.

So, we can have the atomic scattering factor f to be here. And then we have for the first one this one we have e phi i and by now, you know that how it turns out to be and this one comes out to be 0 of course, plus we have this e 2 phi i and then we put this half, half, half. So, what we get h by 2 + k by 2 + l by 2. So, this is the structure factor and then from here what we are getting f equals now, 1 + e phi i into (h + k + l).

Now, what we have to see, we have seen this for bass centered also, how we determine the sign of this f just simply from various combination of this h + k + l and we have derived some general formula. So, we have seen, if this is an even integer of phi i then this will come out to be 1. If it is an odd integer then this will come out to be –1. This e phi i, if it is an even integer so, remember that e n phi i = –1 is to the power n that relationship.

So, from there we know this has to be an even integer of phi i in order to make this one 1 and finally, that will make it 2 f. If it is odd integer, this one n is an odd integer here, this will become –1 and ultimately there will not be any intensity. So, we put that now, that becomes h + k + l. This has to be even and if this is even then F will be only f here it will be f and then we are getting 1 + this entire thing will come out to be another 1. So, we get 2 f.

And the intensity, we know the intensity is basically nothing but mod of F square. So, it comes out to be around 4 F square. This is what the final intensity we are getting, if this h + k + l is even and if h + k + l this is odd. Then what we are getting F = f into (1 – 1) now and this turns out to be 0. So, that means, if h + k + l is even, we are going to get an intensity which is equal to 4 f square.

If h + k + l is odd then we are not getting any intensity for that particular atomic plane. And this kind of planes which basically does not give us any intensity because of the structure factor extraction are called forbidden reflections. These are called forbidden reflections means they are not possible, these reflections are not possible. So, what gives us this combination h + k + l equals even for example, if we took something like 1 1 0, 1 + 1 + 0 is again an odd numbers.

So, 1 + 1 + 0 this has come out to be an even number. This will be giving us an reflection. Second the next one we can check out this is something like 2 0 0. So, 2 0 0 again this is coming out to be even, the third one we can possibly write is something like we can think 2 2 0. So, this will give us another deflection. What will not give that means this condition odd, this will be let us say 1 0 0.

This will be an odd. h + k + l is odd, this will not give us any kind of intensity for the diffracted beam. Then we can have 1 1 1 will not give anything. So, these are the forbidden reflections in case of a body centered crystal structure.

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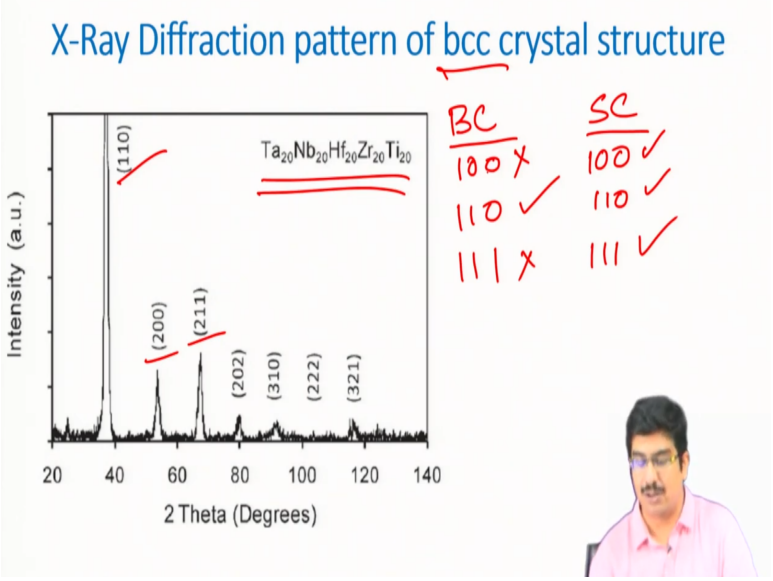

So, let us see, if this is true or not. So, this is now, an extra diffraction from a BCC, body centered cubic. Now, we are dealing with a specific crystal structure and this is a bulk metallic glass, equally atomic bulk metallic glass or this you can see crystalline form of bulk metallic. This is basically a high entropy alloy that that is what you can call. So, if you see, this has the BCC structure.

Of course, if you see the first reflection that we are getting here is basically 1 1 0 then 2 0 0, 2 1 1 again 2 1 1, if you take this h + k + l 2 1 1, h + k + l is 4, so, this is possible. Then the next one 2 0 2, 3 1 0 and so on. So, what you can see here for this BC versus, if you take something like SC simple cubic. So, BC because of this restriction, if I take 1 0 0, 1 1 0, 111. 1 0 0 not possible, 1 1 0 Yes, 1 1 1 not possible again.

If I take simple cubic then we already know that for simple cubic the structure factor is irrespective of h k l. Any combination will give you a certain amount of intensity for this. So, all of them I can have an intensity. So, just if I look at the this diffraction pattern and I somehow get basically I get the peaks for all of this 1 0 0, 1 1 0 and 111. I know it has to be

at least it is not body centered definitely because in body centered case I should not get 1 0 0 or 1 1 1 it has to be something like simple cubic.

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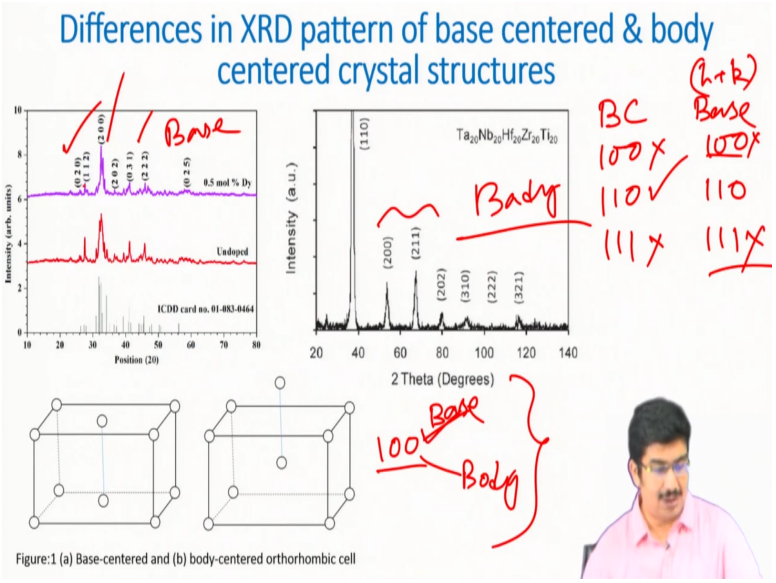

It is not and if we move, if we can see the difference between let us say, again, base centered and body centered the one where we started, if you remember then we were showing that 1 0 0 was this was possible in case of base centered. But this was not possible in case of body centered. If you remember we begin our discussion of diffracted intensity with this example.

And now, we can see the same thing, this is again, this is for base centered, where we are seeing that the 1 0 0 type intensity. This 1 0 0, 0 2 0 basically a variation of 1 0 0. So, this is possible here but 0 2 0, there is nothing like 0 2 0 in case of a BC, this is body centered. So, in case of a body centered, we can again, if we look at this body centered versus base centered then we can see that 1 0 0, 1 1 0, 111.

So, we do not get any 1 0 0. We only get 1 1 0 and 1 1 1, again we do not get it. In case of a base centered, if you remember we are getting 1 0 0 because there the condition is h + k only h + k has to be even, l is not valid here, l is not of any relevance in case of a base center. So, again 1 1 0, 1 1 1. So, which one we are going to get here? This is again sorry, we will not get this one because here h + k we will get the second order one, you will not get this one.

So, 2 0 0 we will get but not 1 0 0 of course. 1 1 0 again we will get it, this 1 1 0 definitely here but 1 1 1 we will not get in case of a base centered. What you are seeing here that we are not getting anything from 1 1 1. We are getting the second order 1 but we are definitely not getting the 1 1 1 for this one. So, again from this diffraction patterns, we can make out some idea about the crystal structure.

Just by looking at which of this diffracted beams which of these diffraction lines are possible in the X-ray diffraction button. From there we can find out the crystal structure.

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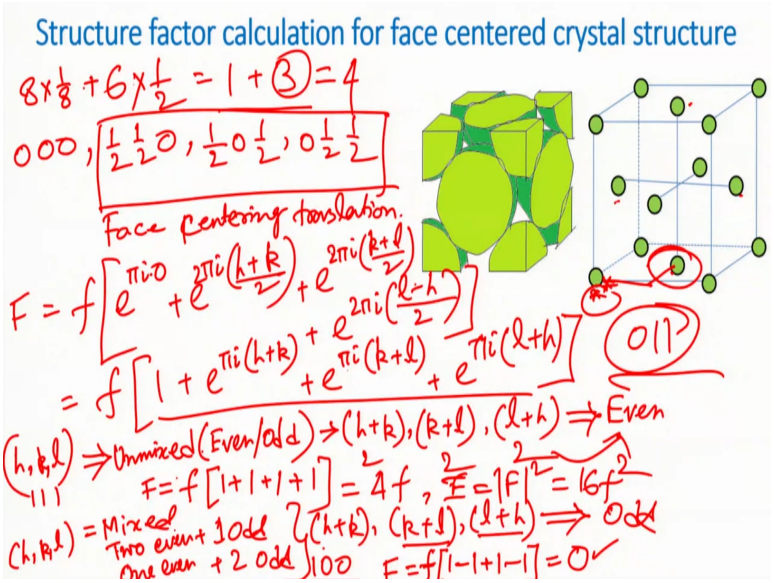

So, this is one way of solving the crystal structure. So now, let us come to this face centered crystal structure. So, face centered again, it is a crystal structure, face centering crystal structure, where you have 8 atoms in the corner. So, those 8 atoms in the corner giving us 1 8 + we have at face center position these, these, these, these and 2 of this. So, we have 6 of this face centering positions presented atoms.

But they are shared with 2 unit cells. So, their contribution here is half all together we have 1 + 3, this many atoms, total 4 number of effective atoms in case of a face centered crystal structure. So, of course this corner one will have 0 0 0, by now, we all know this. Now, what about the face centered ones. So, face centered ones, we can have like this, half half 0 then we have half we have half 0 half then we have 0 half half.

So, these are the general fractional coordinates of the face centered atoms. 3 of this face centered atoms. this is the general fractional coordinate and this one just like body center translation, this is called face centering translation. So, that means, if I start with a corner atom and I apply this let us say half half 0. So, I go half distance here and half distance in the y direction, no movement in the z direction, I will arrive to this space centered atom.

At same thing, if I do in all different directions I will be arriving 2 face centering atom starting from this corner atom. So, this is what the face centric translation means,. So, in this case, again structure factor will be we start with the same kind of atoms. So, atomic scattering factor is amplitude and the first one of course, e phi i into 0 + the second one now, e^ 2 phi i into (h + k) by 2 we can write like this. and what we can write for the other one, e 2 phi i into (k + l) by 2 and the last one will be e 2 phi i and (l + h) by 2. All together it is giving us this F = 1 + e ^into phi i (h + k) + e^ phi i (k + l) + e ^phi i (l + h). So now, what I understand? What we understand? That this entire thing e phi i h + k, e phi i k + l and e phi i l + h this entire one the h depending on the value of h k and l this entire sum this 1 + this entire sum either it will be like 0 or it will be something like a 1 + 1 + 1 + 1 something like that or 1 plus some.

So, some definite value other than nonzero value. So, this one can either have nonzero value or complete 0 value depending on this various combinations of h + k +, h k and l, not h + k + l, h k and l. So, we will be now, considering different combination of this h and h k and l. So, first one we consider then let us say h k l they are unmixed. So, what does unmixed mean? Unmixed means, either all are even, or all are odd.

So, h + k + l either all of them are even or all of them are odd. In that condition, if we consider this unmixed either all even or all odd then what will happen? h + k, k + l and l + h in this condition either all even are all odd they all will turn out to be even. If h + k + l is unmixed that means either all odd or all even then this all of them will turn out to be even how it is done? Let us let us take a quick example that I am taking h k l all to be odd 1 1 1.

All of them are odd 1 1 1 then this h + k will be 2, k + l will be 2, l + h will be 2 and all of them will be even. This is one condition. In that situation F will be f and then this will be 1,

here this is even so, this will now, be an even integer of phi i so, it will be 1, this will be an even integer a phi i 1, this will be an even integer of phi i 1. Ultimately this will be 4f. So, that means I will get an intensity i equals again mod of F square which is now, 16 f square.

So, this is the intensity for this condition. Another condition can be h k l, where this is mixed and mixed means. What does mixed means? They are like 2 of them 2 conditions can happen of course, either 2 are odd 2 even + 1 odd or one odd + or 2 odd one even yes one even and 2 odd. So, what will happen in this condition? h + k, k + l and l + h all of them will be odd.

Whatever you take it. So, if I take let us say this example of this, if I take h k l, what can I take 1 0 0 maybe because 1 is 1 odd 0 0 even. So, in this case h + k 1 and 0, 1, k + l that is this two 0 and 0 this will be now, again here. So, this will be an odd number, this will be an even number but again this will be an another odd number. So, in this case F will be something like f atomic scattering factor into 1 the first one h + k this is an odd number.

So, this is giving me –1. k + l this is again an even number so, this is going to give me a +1 and last one is again –1. So, all together this will be 0, I will not get any intensity from and 1 0 0 plane in case of a face centered cubic crystal structure. So, this I asked you to try so, this one I have tried with this combination to even one odd you can also try it with combination like one even and 2 odds.

Then also it should give you for example, one even 2 odd I am giving you a clue that will be something like 1 even 2 odd. So, this will be something like what it should be 1 even is 0 and 2 odds will be let us say 1 1. So, you can check out this also 0 1 1 another mixed one. So, what should be the intensity and cross check this verify this whether that will be 0 or not.

So, but basically what you understand is that? In case of an FCC or in case of a face centered crystal structure. You will be getting the first reflection from 1 1 1 not from 1 0 0 or 0 1 1 because both of them are mixed.

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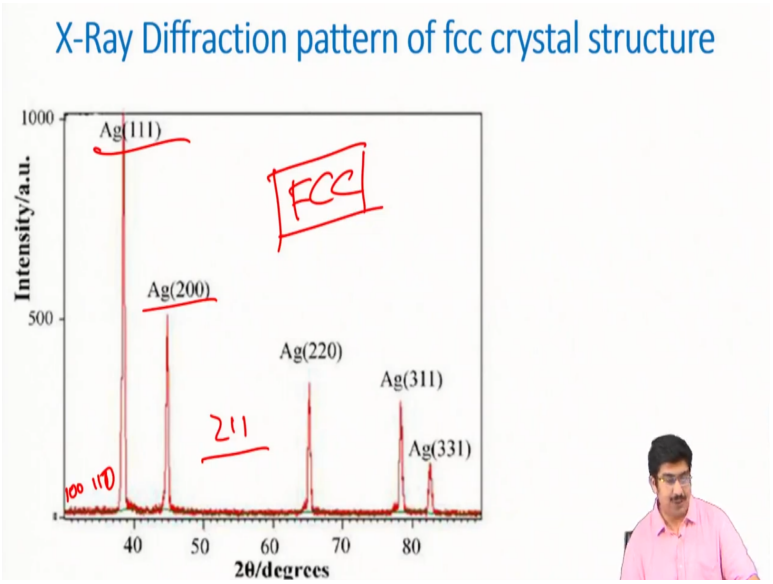

So, this is the condition for an FCC. So, here it is shown for silver, this is an FCC face centered cubic crystal structure. The first one starts from 1 1 1. We do not get any intensity for something like 1 0 0 or 1 1 or 1 1 0. Here, we straightaway start with something like 1 1 1 then next one, we are getting is 2 0 0. Because again can here it is unmixed all of them are even and then we are not getting anything from something like 2 1 1. 2 1 1 is a mixed, we are getting something 2 2 0.

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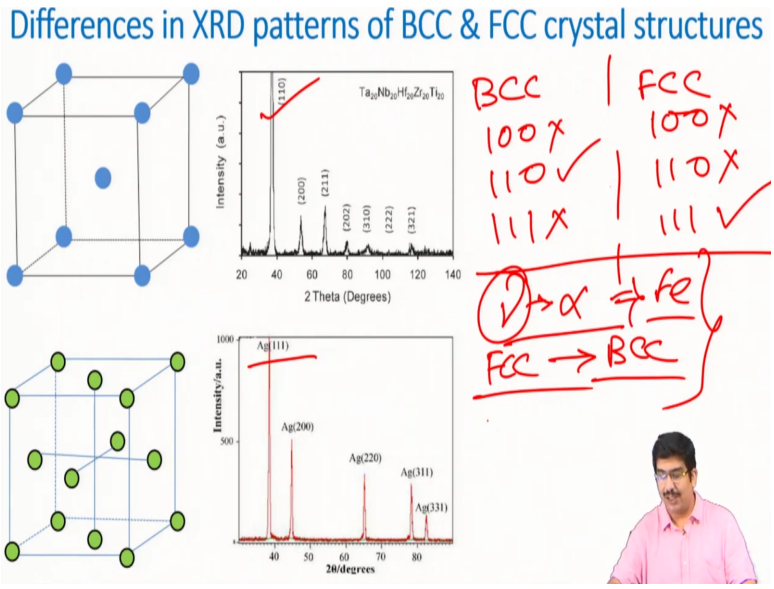

So, if we now, we can compare this with some other crystal structures for example, BCC and FCC. Now, if we compare this BCC and we compare FCC. So, what we are getting here is 1 0 0, 1 1 0, 1 1 1. So, we are not getting this, we are getting this, we are not getting this, in

case of a BCC. For FCC this, this and this, we are not getting this, we are not getting this, we are getting this.

So, this is clearly an difference just by looking at this diffraction patterns and if I can able to solve, I will be able to know a difference and this is very, very interesting, very important. Where if we have something like a phase transformation, the best example of this possibly is something like gamma to alpha transformation. So, where for iron in case of a iron, gamma phase to alpha phase, austenite to ferrite transformation.

So, there what we have is high temperature we have this gamma phase or we have this FCC austenite phase changing to BCC ferrite phase and they are just by looking at this phase transformation the how the change is happening and how this peaks are changing for FCC structure, we will be getting this 1 1 1 peak and slowly as it transforms to BCC structure, we will see that 1 0 0 peak starts coming in.

And then BCC structure again some other peaks higher order peaks also will be coming in. One peak will diminish and other peak will coming out. So, this phase transformation in case of phase transformation this kind of phase transformation, we can very well identify such phase transformation just from taking this X-ray diffraction patterns in different different temperature.

And we will be able to see how this transformation basically changes which plane is giving rise to which plane and lots of things can be done just by simply looking at these peaks or the change in the structure factor.

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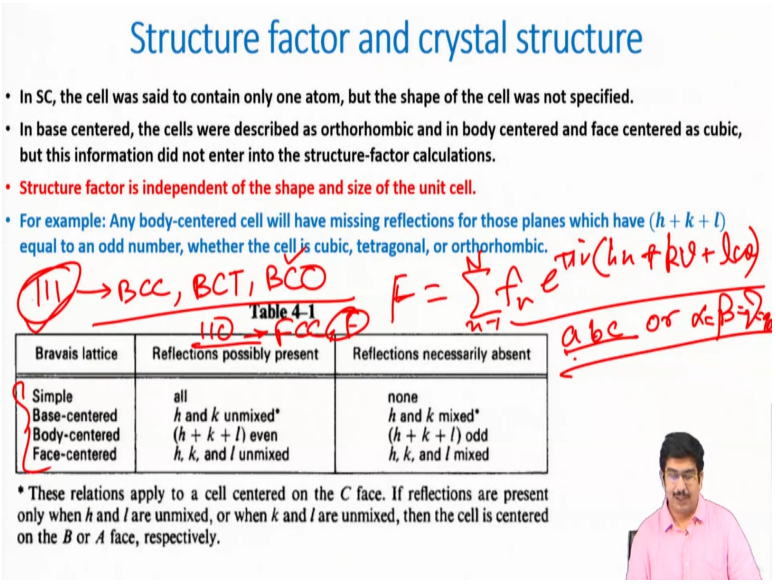

So, structure factor about couple of general things that we must remember about structure factor. So, first of all structure factor, when we are deriving when we derive all of the structure factors, like for simple cubic, like for body centered, like for face centered cubic. What we mentioned is just like the general or the general structure of this unit cell.

We did not mention about the shape of the unit cells. For example, when we said simple cubic, we did not or simple structure, we did not say simple cubic, or so on. When we said base centered we meant orthorhombic but we did not really entered those information like orthorhombic crystal structure a b c, should be a not equal to b not equal to c alpha beta gamma should be 90 degrees.

So, those information did not come in the face center, if you remember the structure factor here again. If I write the structure factor again here so, in the general form of the structure factor, this is the general factor, we understand that this is the general expression for structure factor. This does not contain any crystallographic information. What does this mean? This means that this structure factor is independent of the shape and size of the unit cell.

So, this does not depend on a b c, or alpha, beta, gamma, this angles the structure factor expression does not have anything like a b c or alpha, beta, gamma. So, that means, the base centering can be anything as long as it is orthogonal. Of course, if it changes this

orthogonalities change then the structure vector expression will definitely change. But, as long as it is an ortho normal that means, alpha, beta, gamma = 90.

If we consider this, it does not depend on a b c, whether a b c is equal or not equal, it does not depend on that. That means, the body centered cell will have any kind of body center, if it is a body centered cell, any kind of body centered cell will have missing reflections form h + k + l, if h + k + l is an odd number then that will not be coming in the extra diffraction pattern. Whether the unit cell is cubic tetragonal or orthorhombic. That is it.

So, that is what, so, for example, what we mean here is that if I just think about 1 1 1 reflection. So, this 1 1 1 reflection will not be there, whether it is a body centered cubic or body centered tetragonal or body centered orthorhombic. Whatever be the structure, just body centering; simple body centering will make this intensity from this crystallographic plane to disappear.

It does not need to or it will not be a special case for what is in the cubic or body centered tetragonal or body centered orthorhombic. It will offer all cases this will be not their similar thing for face centering, we have already seen that in case of face centering, we did not have anything like something like 1 1 0. So, 1 1 0, whether it is face centered cubic or face centered tetragonal is not there but any other face centering case does not matter, it will not be there.

So, this is this relationship that we have derived here is very much general and it does not depend on the particular unit cell that we take. It does not it is so, general structure factor is independent of the shape and size of the unit cell.

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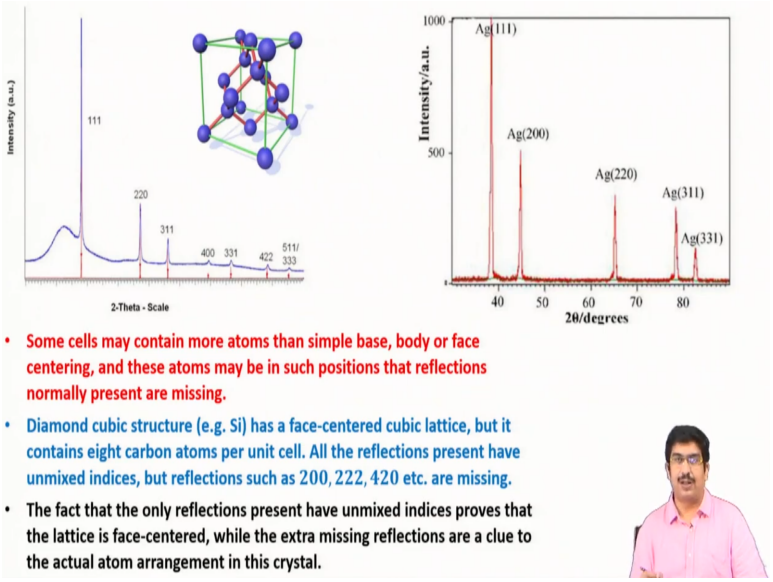

So, another thing that we need to discuss is that certain cells, if we go for a more complex crystal structure. Then structure factor modifies even more other than this relationship that we already derived other than this relationship, there has to be some more relationship or there are more ways of modifying the intensity, if some certain reflections are absent which are possible with a simple calculation structure vector calculation.

Additional conditions are coming up, additional conditions are controlling the intensity of the diffracted beams in case of more complex crystal structure. This we will take some particular examples. For example, like diamond cubic structure in case of silicon and we will be also discussing possibly the structure factor of NaCl crystal structure in the next class. So, bye.