Techniques of Materials Characterization
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Lecture – 52
Intensity of diffracted beam (Continued)

Welcome everyone to this NPTEL online course on Techniques of Materials Characterization. We are in module 11 and we are continuing with X-ray diffraction basically, we are continuing with intensity of diffracted beam. In the last class, we have talked about the structure factor calculation, we have derived an expression of structure factor and in this class we will be continuing with calculation of structure factor for various crystal systems.

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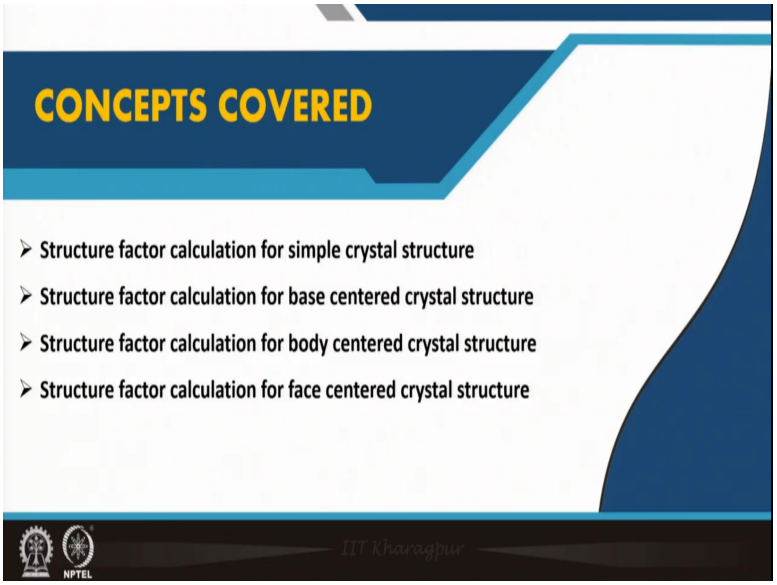

We will start with a simple crystal structure then we will go for a base center crystal structure, body centered crystal structure and face centered crystal structure and we will try to show the differences similarities of this various structure factor of this various crystal structure.

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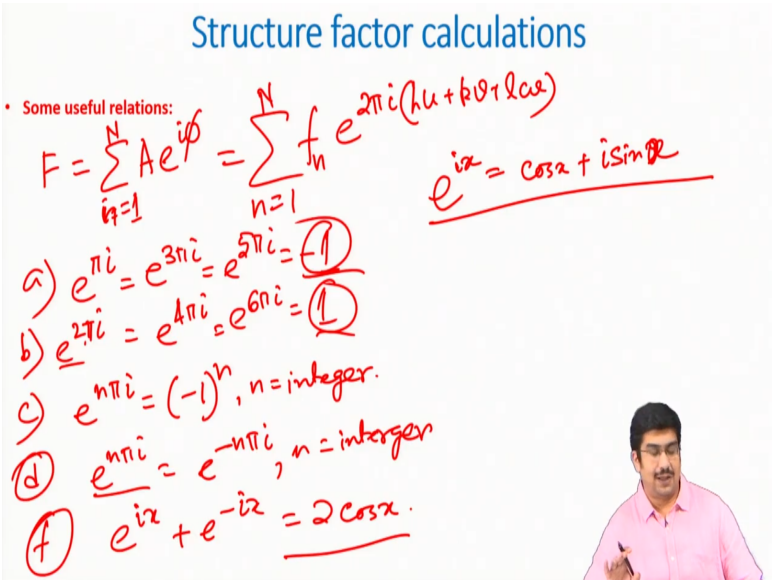

So, before we begin basically let me again give you a quick recap and derive some useful relations about structure factor. So, if you remember we have derived the structure factor in this way basically we said the structure factor is it is, the way it is I think there is a problem here out check it out and the way we can derive, we can define the structure factor is basically this.

Where for n number of atoms we take a summation of these waves that is scattered by each of them that is deflected coming out of each of these atoms. And finally, we are saying that this one, if we express this again in terms of the particular phase and amplitude. So, amplitude is basically represented by the atomic scattering factor whereas, phase is represented we have already derived it is represented by this relation 2 phi h u + k v + l w.

Basically through the fractional coordinates of this second atom here. So, some useful relations; that we that will help us to derive the specific structure factor relations for various different types of crystal structures. So, we will be writing it here, number 1, first and these are basically simply simple mathematics, this is nothing special. This is simple complex number mathematics and simple equations for power series expression.

So, if we have something like this, e raised to the power phi i = e raised to the power 3 phi i = e raised to the power 5 phi i, ultimately this all boils down to –1. Then the second one that means, if phi is an integer multiple of the center there is an integer i and then there is an

integer multiple of this which is even here which is odd. Now, we will see, if that is an even so, if we have an even multiple of i then what will happen this like e 2 phi e 4 phi i and then we have e 6 phi i all of this will be 1.

So, the general rule that we can write down is basically e n phi i will be –1 is to the power n, where n is an any integer. And also, we can write this is 1 and also another one we can write e equals n phi i equals e equals – n phi i. This is also is valid where again n is any integer. So, what this one means basically? This one is like e n phi equals –1 raised to the power n. Let us say n is 1, 3, 5 all of this that means –1 raised to the power 1, 3 ,5 in that case, it will be –1.

So, if n is a odd number then, it will come the value will be –1, if n is an even number the value ultimate value of n phi i will be even number. So, or it will be 1 and if it is odd number odd multiple of phi then this will be then this will be –1. And also we can convert e n phi i and e n – phi i is the same. That means, e being any integer. So, e phi i = e – phi i.

So, that is another very important relationship and the final relationship that we can write which will be useful for us is basically e into i x, e ^i x + e^ – i x = 2 cos x. This is basically the way e is explained, if you remember e phi x is equal to what we said e i x is basically expressed as cos x + i sinx. This is how the complex numbers are basically expressed. So, if you add them up then you will be getting the same.

So, these are the very useful relationships that we will be using while deriving the structure factor for various atom, various crystal systems.

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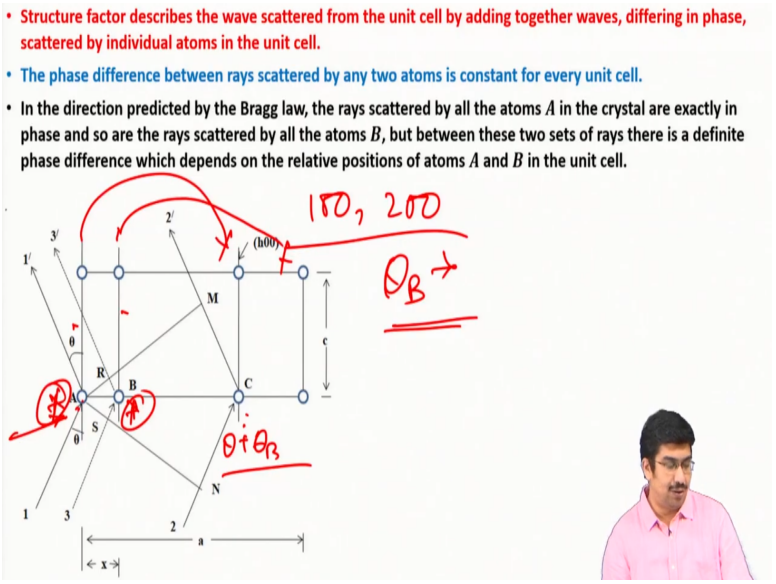

So, one thing before going there one final thing about structure factor that we must understand is that the structure factor basically describe the waves scattered from the unit cell by adding together waves. And waves which are coming from different atoms just like here we are adding up one wave coming out from this set of plane h00 plane and the waves coming out from another set of plans B.

Which are having a differing n phase and may differ may or may not differ in amplitude that does not mean. But the point here important point here is that there is no phase difference between the rays coming out from A and C. These 2 planes this h 0 0 planes between the h 0 0 planes. For example, if I take 1 0 0 planes and 2 0 0 planes, there is no difference between their faces that is what.

And they may have a phase difference between this set of planes and this set of planes but individually between them there is no difference in place that is the assumption of calculating the structure factor. Basically this is not very true because we know that as we are in X-ray diffraction after certain we make the next module. We will discuss or in during discussion in electron diffraction we have seen that the Bragg's condition is also satisfied for and this theta B, the angle for which the Bragg's condition is satisfied.

This has a range this is not an exact angle this is there is a finite range of because of which we have seen that the wall sphere touches when it becomes a cylinder the points become

cylinder. And so on, in case of electron diffraction similar things we will be seeing in case of an X-ray diffraction, where it leads to a broadening of the peak. But basically, this diffraction conditions are satisfied for a range of angle not only at a single Bragg's Law, Bragg's point.

So, that is why they are the waves that are generated between this atomic plane and another atomic plane, this can be for an angle of theta + theta B. A little bit deviation can be there but when we calculate the structure factor, we safely can ignore this. And we can just imagine that the structure factor represents basically the waves coming out from one set of plane which does not have any phase difference between themselves.

And another set of plane which again does not have. So, this setup plane and this setup plane, they will not be having any phase difference between them. So, only between themselves they will be having a phase difference. So, this is an important point to consider and we should not get confused later when we discuss about this phase broadening and so on.

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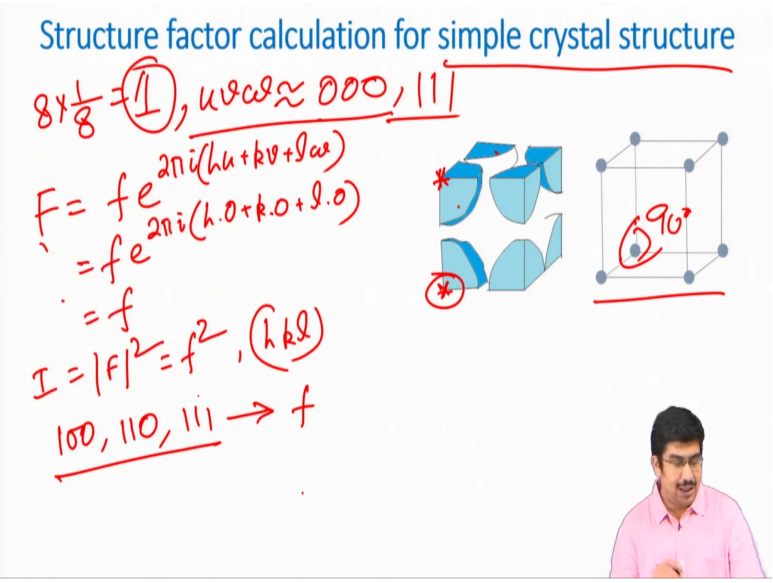

Now, let us forget all of this and let us start doing some simple very simple and fun things, calculation of structure factor for various types of crystal system. So, this is a simple crystal structure. So, simple crystal structures, how do we define a simple crystal structure? Basically, a simple crystal structure has, if we consider something like an orthogonal crystal system. That means this angles we imagine that all of these angles are 90 degrees.

So, this is a simple so, we could imagine that these angles are not 90 degree. But that will be just little bit more complex to understand. So, we imagine that this is a simple structure and all these angles are like 90 degree to each other. And a simple structure is defined with atoms in all different corners. So, this is not a closed pack structure. So, atoms in all different corners and these atoms are basically shared with each other such unit cells.

So, we have 8 atoms in 8 corners and all of these atoms are shared with 8 other unit cells. So, their individual contribution is 1 by 8 and finally that means the effective number of atoms within this simple unit cell is 1. Now, the fractional coordinates that is u v w, we can represent this for this one. If we represent this let us say 0 0 0 that is this origin, if we think that this is the origin, so, another atom will be here.

So, this another atom anywhere this one, this one, this one, this one anyone. So, the another atom should have its fractional coordinates at 1 1 1. Point is this 0 0 0 and 1 1 1 basically will be can be interchange. I can just simply shift the origin here and then this atom which I was like imagining that this is 1 1 1 now, becomes 0 0 0. So, that means effectively this u v w here is we can write for all kinds of atoms in this structure.

The u v w the fractional coordinates for them will be 0 0 0. one single atom at fractional coordinates of 0 0 0 that is what nothing else. So, or other way around we can say that this is let us say 1 0 0 plane is this. There is nothing in between the, another plane is another type of 1 0 0. So, if we draw something analogy with this, what we are doing here we have just this one set of plane present here.

There is no other atom, no other plane present in the entire calculation nothing comes in between. So, the structure factor of this simple structure is also comes, if we write this F equals and we imagine that 1 single atom this has 1 single atom there is no difference between the atoms, if these atoms are of 2 different types. It is not a simple structure crystal structure it will become some other type of crystal structure.

So, we imagine all of this atoms are of the same type and then their amplitude, it can simply be represented by their atomic scattering factor and then we can write for them the expression

because, f * 2 phi i *you know this h u + k v + l w. And since u v w = 0; what we can write, if 2 phi i h into 0 + k into 0 + l into 0 finally comes down to be f. That means the intensity which is basically nothing but square of the modulus of structure factor simply will come down to f squared.

So, what does this mean? This means that for every kind of h k l, any diffraction condition for any kind of plane be it 1 0 0, be it 1 1 0 be it 1 1 1, any kind of plane we will be getting an intensity, some amount of intensity. None of these planes or none of these diffracted beams will be absent, all of them should be present in the x-ray diffraction pattern because for all of them, because what is it means that structure factor basically the expression of structure factor.

It does not contain any particular expression from the atomic positions or the plane itself. So, that means all for all possible planes all possible h k l. There will be certain amount of intensity which is expressed by this f squared term.

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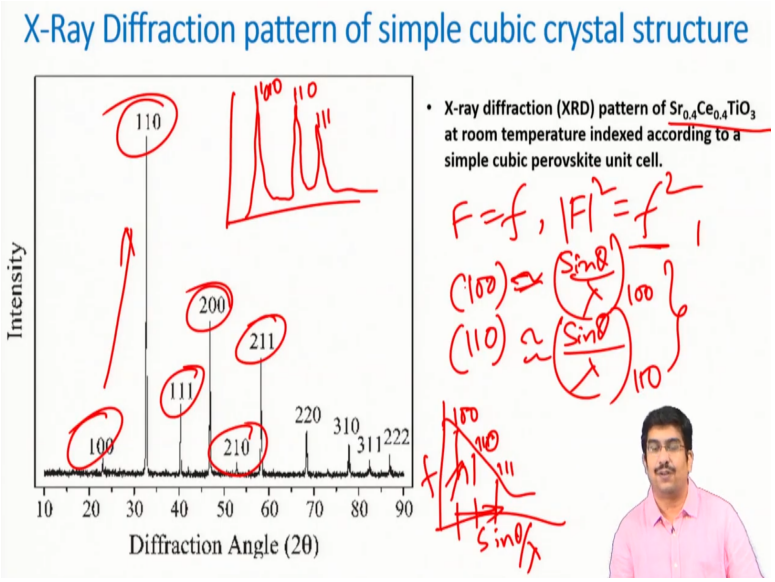

So, let us see then this x-ray diffraction pattern of a simple cubic structure. So, this one is given from a perovskite structure simple cubic perovskite unit cell strontium, cerium, titanium. And here, if you see, you will see that there are all different all kinds of planes are present 1 0 0 is present, 1 1 0 is present, 1 1 1 is present, 2 0 0, 2 1 1, 2 1 0. So, there is no restriction on any kind of diffraction plane, any kind of diffracted beam.

All possible diffracted beams are present here and the intensity is simply wearing as f square. Now, you can see there are huge difference in intensity between this peak and this peak and this peak. This is coming for other factors which we will discuss later, this kind of intensive difference but from structure factor calculations that is since we know that F = f this basically the intensity will be simply a square of the atomic scattering factor.

The way atomic scattering factor varies and atomic scattering factor of course, one more thing you should remember here, the atomic scattering factor for 1 0 0 planes and 1 1 0 plane is not the same. Because sin theta by lambda for 1 0 0 plane, sin theta by lambda, lambda being constant. Let us imagine the lambda constant but still sin theta is changing. So, even if lambda is constant sin theta for this 1 0 0 plane and this one 1 1 0 plane will be different.

Sin theta is increasing here. As you know, from this relationship, if you remember this relationship between the atomic scattering factor and sin theta by lambda in phi, it varies like this. So, if you are moving in this direction the atomic scattering factor is also decreasing. So, that means, ideally from 1 0 0, it should continuously decrease. If there is no other effect; that is why I said that there are many other effects, if there is no other effect.

Then the intensity of these peaks will simply decrease as per atomic scattering factor but there are many other factors which is controlling this intensity of this diffracted beam. So, if there are no other factors no other things are controlling the intensity of this. So, then what we should get, the 1 0 0 peak should be the maximum intensity then the next intensity should be 1 1 0 and the next intensity should be 11.

So, this will be 1 0 0, this is 1 1 0, this is 1 1 1. So, this way, it should vary as per this because here atomic scattering factor, if we look this is possibly 1 0 0, this is 1 1 0 and this is 1 1 1. This is for sin theta by lambda from there. So, intensity also should vary in that same way but it is not happening even for a simple cubic, it is not happening simply because the diffracted beam intensity depends on many other factors some of them which we will be discussing in the next few classes.

So, this is first simple cubic structure where we understand that all the diffracted beam from all kinds of atomic planes are possible.

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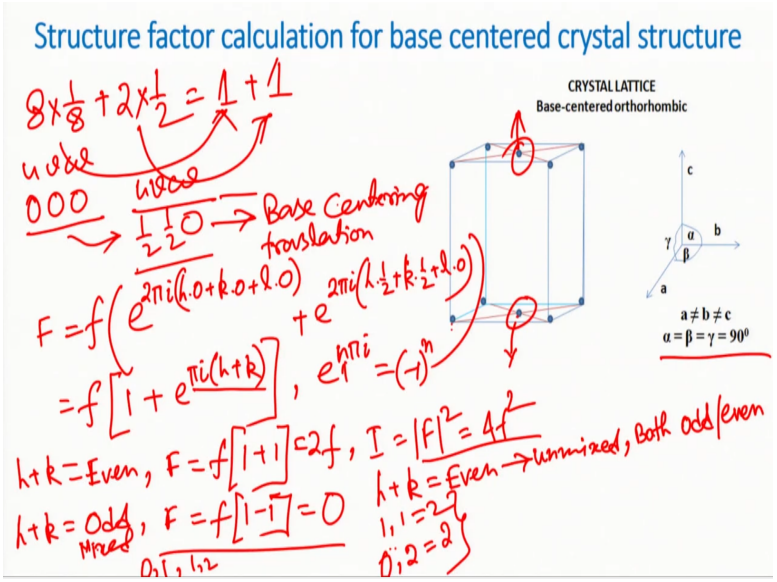

Now, let us calculate for another kind of crystal structure base centered. So, what is the base center crystal structure? If you again let us imagine that same thing that we are basically base centered crystal structure is most prominent in base centered orthorhombic crystal structure. That is why we have written that this is we have imagine a special case that this is base centered orthorhombic crystal structure where a b c, a not equal to b not equal to c but alpha beta gamma equals 90 degrees.

So, this contains 2 sets of atoms as we can understand. One set of atom is basically forming the corners again 8 corners and they are giving 1 eighth contribution plus I have 2 different atoms one here and one here. So, 2 different atoms and they are giving they are shared these 2 are shared with another unit cell. So, this is shared with another unit cell in below this, this is shared with another unit cell which is above this.

So, their contribution will be half all together I will be having 1 + 1. So, 1 atom that is coming out of this cornered cells and 1 atom effectively that is coming out of this base centered position. So, how do I define these 2 atomic positions? So, of course, the 1 which is in the corner we have just seen from simple cubic, if anything is in the corner, we can simply write it fractional coordinates this is basically u v w as 0 0 0.

What about this? For this u v w will be something like what we can write 1/2 1/2 0. So, that will be the fractional coordinate you can check it here. So, if you move half distance in the x direction then you move half distance in the y direction, half means half of a. So, if you move half of a here, half of b here in this direction and no movement is needed in the c direction you will be reaching to this bass center atom.

So, that is why I said that this is the position for base centered atom and this is called base centering translation. So, if you start with the 0 0 0 corner atom and then you apply this base centering translation on this atom you will be reaching to this base entry position that is what. So, simply again we will be doing the same thing we will use the same expression for f equals.

Now, we imagine that again they are of same type we do not go into complexity, we just imagine that all of them are the same type of atoms. So, we simply have this multiplication with the atomic scattering factor and for this atom. For this base atom what we have 2 phi i into h into 0 + k into 0 + l into 0 plus we have this base centering atom. For that we can take 2 phi i h into half + k into half + l into 0.

All together what we will get is f into 1 + e ^ phi i into (h + k). If you solve this one this is ultimately the expression that we receive for a base center the structure factor for a base centered crystal structure. Now, what happens here? We have already done this useful relationship we know that what, it should take this this value. For even so, if we now, imagine that h + k, 2 different conditions can happen.

Either h + k can be even or h + k can be odd and depending on that this entire expression will change. So, if h + k is let us say we imagine that h + k is even then F what will happen to F? This will happen h + k is even that h this thing F will be so, we know that if for even this comes out to be e we know this e n phi i = –1 n. So, that means, if this is even then this is +, this is – i this is + sorry this is 1, if n is an even number then this is 1.

So that if this is a, this one is an even number this h + k is even number then we get F = 1 + 1 that means, it is 2 f. And intensity in that case I will be equals to again F square that will be 4 f square. So, this is for h + k even. Now, how we can have h + k even and if what also we will see that if what will happen if h + k equals odd. Then again what will have F = f into (1 – 1) from the same relationship 1 – 1 = 0.

So, I will not get any intensity from this. Now, we have to solve it a little more. How we can make h + k? h + k = even. So, this is possible when we have h and k unmixed that means unmixed. What does it mean? Unmixed means either h and k both odd or both even. So, both that means;, both odd or both even. If this is true then this will be h + k will be even that means, either we can have both odd or both even, if they are both odd.

Let us say both odd means they are 1 and 1, it will be 2 = 1 and 1 + 1 = 2, or both odd and odd means and in this calculation we will be imagining 0 also as a even number, we will start the even number not from 2 but from 0. So, let us say h and k one is 0 and one is 2. Again, if we add them up that will be 2 and that means that will be an even number.

So, this means finally the relationship comes down to be h k either both even, they should be unmixed, either both even or both odd in that case, I will be getting into reflection, I will be getting the diffraction and this will be their intensity and on the other way. If h + k, the way they can go for odd is basically, if they are mixed. That means one of them is even and one of them is odd.

If they are mixed then there h + k is odd and I will be getting no intensity at all that means mixed means one is let us say 0 1 and or otherwise, we can imagine that one is 0 and one is 1 or one is 1, one is 2, so on and so forth. So, these kind of combinations will give me no intensity at all even though the Bragg's condition is satisfied that then also we will not get any intensity from those particular atomic planes.

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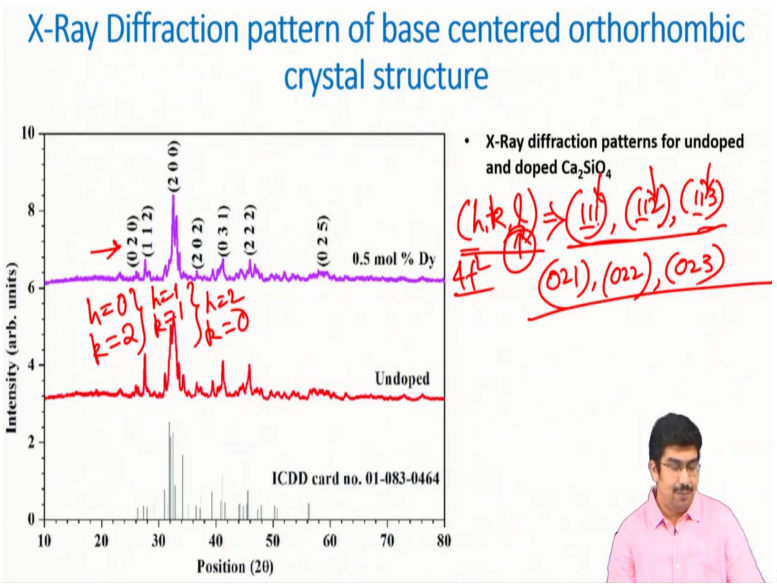

Now, one thing you must understand. Let us see this crystal structure for a base center orthorhombic crystal and you can see that we are getting intensity. First intensity we are getting from 0 to 0 that means here h = 0 and k is 2. So, we are getting, an intensity from there. Next one we are getting where h = 1, k = 1, the third one we are getting 2 0 0, h = 2, k = 0.

So, all of these cases this is unmixed that means, both of them either they are both odd or they are both even. Either they are both even or they are both odd. But we are not getting from any of the conditions we are not getting where they are unmixed. So, if they are mixed, we are not getting any kind of diffraction from those kinds of structure. But one thing you must notice here is that only important points are h and k not the l.

So, l is can be independent, in this case. The l value of l is not at all important in this for calculating for the base centered condition. So, we can have reflections from any combination of h and k. And we do not need to bother about l at all. For example, so, l is not at all important in calculating the intensity. In this case, for example, if we have something like 1 1 1, if we have something like 1 1 2, if we have something like 1 1 3, all of them will have the same intensity, because h and k are the same.

So, all of them will have an intensity of 4 f square, the l value does not make any difference because their h and k value is important here. Similarly, we can imagine that something like 0

2 1 or 0 2 2 or 0 2 3 all of these planes will have diffraction and will with the same kind of intensity as per the structure factor. Of course, as I said the structure factor is not the only factor which sort of depends or which controls the intensity final intensity.

There are other factors but as per the structure factor calculation, all of these planes will have the same intensity for the diffracted beam. It does not matter what l value the final one, what is the l value, it does not matter at all, only the first 2, h and k matters for this kind of calculation.

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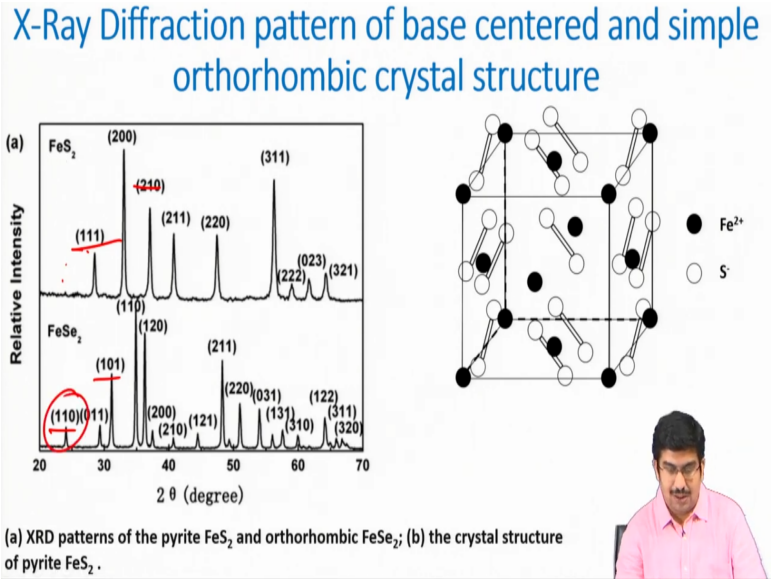

So, now, if we calculate if you compare the X-ray diffraction pattern from a base centered and a simple orthorhombic, it will become much more clearer. So, base centered one the simple the base centered one is given here and I think the simple orthorhombic is this one, the bottom one is simple orthorhombic for iron sulfide and iron selenide. So, iron sulfide is a orthorhombic based center orthorhombic crystal structure.

Whereas, iron selenide; is a simple orthorhombic crystal structure. So, you can see for iron sulfide which is base centered one, this you are getting diffraction from 1 1 1 peak you are getting from 2 0 0 planes you are getting it from 2 1 0 plane. Okay!, This is a little odd because it should not get what 2 0 0 planes but anyway, there must be some other factors. But iron selenide which is basically the normal orthorhombic simple orthorhombic.

You are getting from 1 1 0 planes which is not allowed for Fe Se, so, 1 1 0 planes. No, this is a little problem, I think!. So, we will stop I think here but we will be continuing with this structure factor calculation for body centered crystal structure and all other crystal different other crystal structures. We will be continuing with this in the next class. Thank you.