Techniques of Materials Characterization
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Lecture – 54
Intensity of diffracted beam (Continued)

Welcome everyone to this NPTEL online certification course on Techniques of Materials Characterization. We are continuing with X-ray diffraction, we are in module 11 and this lecture will again discuss about the intensity of diffracted beams. So, the previous lecture we have derived structure factor expression and we have discussed the structure factor what are the conditions of getting something diffracted beam from certain crystallographic planes.

We have seen that condition, we have developed the condition for simple and then base centered, body centered and face centered crystal structure and we have seen, we have told that the conditions because of which certain intensities certain input which are known as the forbidden reflections are missing in case of body centered, in case of face centered those crystal structure and how we can utilize this in order to study something.

For example, phase transformation and also we have discussed about the general nature of structure factor calculations that this body centering or face centering. This is independent of the crystal structure that we take.

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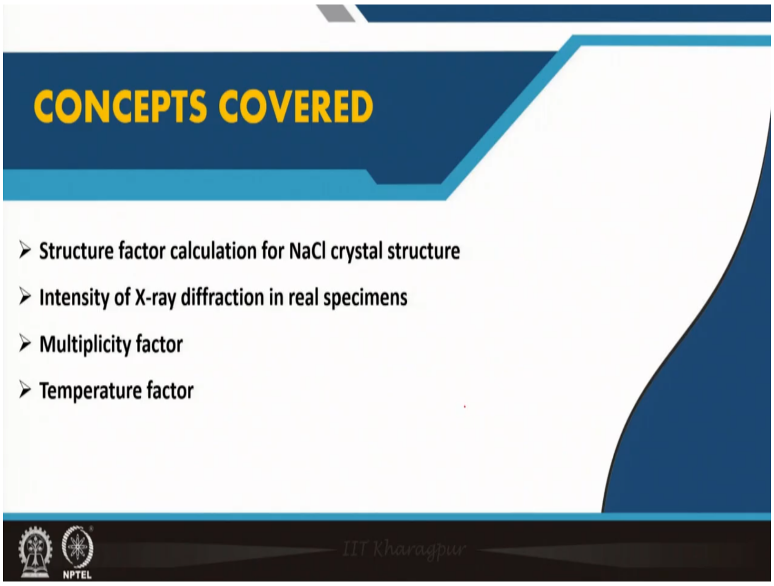

CONCEPTS COVERED

- Structure factor calculation for NaCl crystal structure
- Intensity of X-ray diffraction in real specimens
- Multiplicity factor
- Temperature factor

So, in this class, we will continue with that and we will discuss about the structure factor calculation for a more complex crystal structure NaCl we will take one. And then we will see the intensity of X-ray diffraction in a real specimen what are the other factors that this intensity X-ray diffraction intensity depends on in a real sample. And we will try to discuss about at least multiplicity factor, temperature factor possibly in the next class we will discuss.

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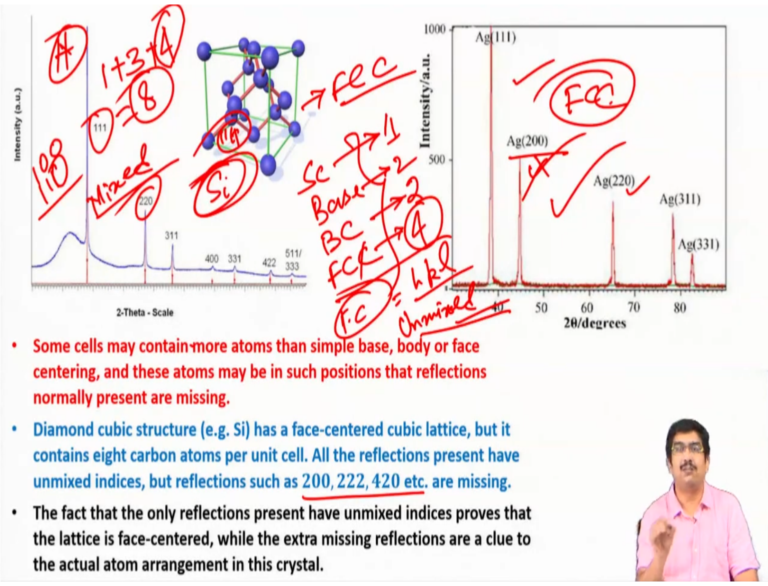

- Some cells may contain more atoms than simple base, body or face centering, and these atoms may be in such positions that reflections normally present are missing.
- Diamond cubic structure (e.g. Si) has a face-centered cubic lattice, but it contains eight carbon atoms per unit cell. All the reflections present have unmixed indices, but reflections such as 200, 222, 420 etc. are missing.
- The fact that the only reflections present have unmixed indices proves that the lattice is face-centered, while the extra missing reflections are a clue to the actual atom arrangement in this crystal.

So, we will continue with our discussion about the structure factor for more complex crystal structures. For examples, until up to now, we have discussed or we have derived the conditions for 4 different structures and those 4 is like simple BC bodies or base centered and body centered and face centered. So, here the maximum number of atoms that we discussed is 4 in case of FCC.

Body centered is basically we discussed about 2 base centering again, we had only 2 and simple one only 1. So, what if the structure contains more number of atoms than this more number of atoms then 4. So, those kinds of cells like will be in such a way so, the atoms, if the unit cell contains more number of atoms then this FCC then the face centered condition then we will have some additional restrictions on the diffracted beam intensity.

So, diffracted beam other than this for example, if we derive like face centered the conditions that h k l has to be even all unmixed in this condition on and above this condition. We will have some other conditions for getting intensity or which will be modifying the intensity of beams from certain crystallographic planes**.** So that will have further restrictions or the intensity of those beams will be further modified.

So, for example, if we look at this diamond cubic structure, this is the silicone best known example is silicon diamond cubic. So, diamond cubic unit cell is the basically it is an FCC structure is and then additionally we have some other 4 other atoms within the unit cell which are basically present in the tetrahedral void positions, 1 forth and 3 forth position, 1 forth and 3 forth of body diagonal.

So, this positions we have additional atoms and out of the 8 position only 4 are there. So, this is the diamond cubic structure. So, diamond cubic structure based on example, is silicon and in diamond cubic structure, we will have corner atoms + 3 presented atoms + 4 additional atoms. So, altogether it has 8, effective number of atoms is 8. So, in diamond cubic structure will have like this is the typical FCC structure.

And in this case in addition to that we will have some other reflections like 2 0 0, 2 2 0, 4 2 0 this kind of reflections will also be absent. So, we will be having the same that unmixed. So, the mixed one in this case the mixed one will be absent for because it is basically an FCC structure. So, this restriction will be there for diamond cubic structure for silicon structure, this restriction will anyway be there.

That mix reflections in any case like for example 100, 110 and so on. This kind of mixed reflections will not be there. So that will be the same as FCC but because of the presence of this additional 4 atoms here, what we will be not getting? We will not get some more reflections for example, 2 0 0 unlike this normal FCC where we have after 1 1 1 we have the second one as 2 0 0.

In case of silicon after 1 1 1, we will have the next one as 2 2 0 which is here. So, this 2 0 0 is completely absent in case of diamond cubic because of those 4 additional items. The structure factor gets modified even more. We are not going in the exact form of that structure factor determination you can try that at home as an assignment. But, we will find out that not only mixed unmixed condition, there will be far more other condition.

Basically one of these conditions I was discussing in the last class, if you remember. Even within the mixed condition to even + 1 odd versus 1 even + 2 odd. What is the difference between then and there? This diamond cubic structure that will be very important you can try that. So, but the fact that in case of a diamond cubic structure, this basic condition is valid the mixed condition, mixed unmixed condition is valid.

That means, if it is a mixed then you will not get intensity anywhere. Whether it is an FCC, whether it is a diamond cubic, you will not be getting intensity. So that itself means that this lattice is by default, it is a FCC. So, the base is FCC and on top of the FCC structure there are more modifications because of extra atoms present. So that if we solve, if we get anything like this kind of reflection.

Then we know that we have to start the atomic unit cell, if you want to construct the units and if you want to solve the crystal structure, we should start from something like an FCC units and then on top of the FCC unit cell because of some other restrictions, we have to put some other atoms in proper place.

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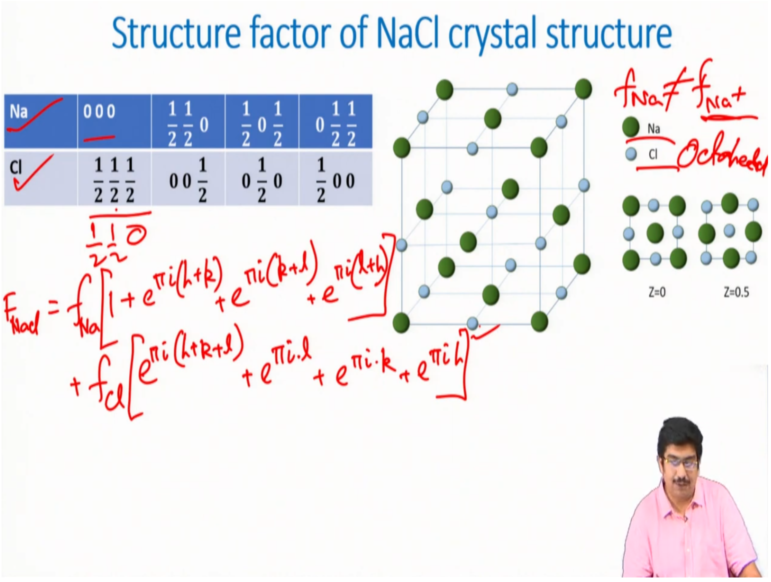

Structure factor of NaCl crystal structure

Na ✓	0 0 0	$\frac{1}{2}\frac{1}{2}0$	$\frac{1}{2}0\frac{1}{2}$	$0\frac{1}{2}\frac{1}{2}$
Cl ✓	$\frac{1}{2}\frac{1}{2}\frac{1}{2}$	$00\frac{1}{2}$	$0\frac{1}{2}0$	$\frac{1}{2}00$

$\frac{1}{2}\frac{1}{2}0$

$$F_{NaCl} = f_{Na}\left[1 + e^{\pi i(h+k)} + e^{\pi i(k+l)} + e^{\pi i(l+h)}\right] + f_{Cl}\left[e^{\pi i(h+k+l)} + e^{\pi i \cdot l} + e^{\pi i \cdot k} + e^{\pi i h}\right]$$

$f_{Na} \neq f_{Na^+}$

Octahed

So that is how the structure factor for this complex systems is again related to their unit cell or the atomic arrangement within the unit cells. So, we will take one specific example or more famous example here that will make this what we are discussing more clear that on top of FCC crystal or FCC structure factor relation, what other factors are will come and modify the intensity.

So, as it is shown here, this is the atomic positions for sodium and chlorine. So, this is sodium, if you consider only sodium, this is an FCC. So, we have this as the sodium. So, the green balls are sodium and sodium itself has its own FCC structure, proper FCC structure. Now, chlorine, if we consider here chlorine will also have its FCC structure basically chlorine lives in the position of octahedral voids which, if we join the sodium the chlorine atoms here.

We can construct another FCC lattice from this of course, we need some other unit cell on sides then we can join and we can construct a unit cell, FCC unit cell of chlorine itself. And in that case, sodium will be in the octahedral void position. So, whatever it is so, basically what we can call that sodium and chlorine both forms their own FCC structure which are interpenetrated and sodium position of sodium and chlorine is quite interchangeable.

So, face centering translation again you have for sodium position, you have the face centering translation, chlorine positions also you have the face centering translation. If you just you have to the nature of the face centering translation is a little different. So, you just add the face centering translation with this. What you are getting is this one. You are basically shifting the origin, you can shift the origin.

So, if you just add along with that you add this face centering translation, half half 0, you are getting basically 0 0 half, this will become 1 1 1. That you take that as an origin shift and you will be getting this again this one. So, chlorine and that is why I say chlorine and sodium positions are very much interchangeable. But that is okay. Let us not go into there and let us try to solve this particular problem of NaCl structure factor of sodium chloride.

So, I write again structure factor F for this complete sodium chloride NaCl structure. Then I write the here the question comes sodium and chlorine, I have 2 different type of atoms. So, their atomic scattering factor will not be the same. I can write 1 as sodium. Now, here the point is, actually sodium structure factor of sodium is not equal to or atomic scattering factor of sodium is not equal to atomic scattering factor of sodium N +.

Because N a + is what we are getting in NaCl. There is a difference basically here there is one electron is removed from here and that is why it has gotten to the ionized condition same way chlorine has received one electron and it has gone to ionized. So that means the atomic scattering factor of sodium atom, pure sodium atom and sodium chloride Na + ion is not the same.

But, anyway we are not considering that we will just be writing it Na whatever it is Na + or Na we will write. So, atomic scattering factor of sodium and then we know how to get that later part the face part and we are writing it as 1 + e phi i. So, this is typical for an FCC the one that we have already derived. So, + e phi i into k + l + e phi i into l + h. So, this is what the expression for sodium.

And now, we have to write the expression, similar expression for chlorine and that will come a little different because of the atomic positions or you can interchange also. Because of the atomic position it will be a little different but ultimately it will boil down to the same, we will see how. So, this one will be phi i into h + k + l + e phi i into l + e phi i into k + e phi i into h, you can put all of this and you can find out.

So, now, from this so, this is the entire structure factor for this sodium chloride structure. And this to looks quite different but they are not we will see how.

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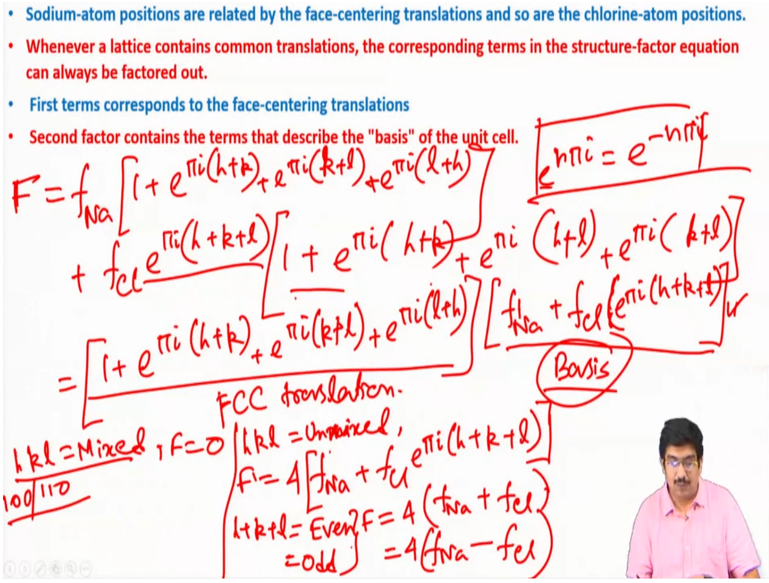

- Sodium-atom positions are related by the face-centering translations and so are the chlorine-atom positions.
- Whenever a lattice contains common translations, the corresponding terms in the structure-factor equation can always be factored out.
- First terms corresponds to the face-centering translations
- Second factor contains the terms that describe the "basis" of the unit cell.

$$e^{n\pi i} = e^{-n\pi i}$$

$$F = f_{Na}\left[1 + e^{\pi i(h+k)} + e^{\pi i(k+l)} + e^{\pi i(l+h)}\right] + f_{Cl}\, e^{\pi i(h+k+l)}\left[1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}\right]$$

$$= \underbrace{\left[1 + e^{\pi i(h+k)} + e^{\pi i(k+l)} + e^{\pi i(l+h)}\right]}_{\text{FCC translation}}\underbrace{\left[f_{Na} + f_{Cl}\, e^{\pi i(h+k+l)}\right]}_{\text{Basis}}$$

hkl = Mixed, $F = 0$

100, 110

hkl = Unmixed, $F = 4\left[f_{Na} + f_{Cl}\, e^{\pi i(h+k+l)}\right]$

$h+k+l$ = Even, $F = 4(f_{Na} + f_{Cl})$

= Odd, $= 4(f_{Na} - f_{Cl})$

So, basically what, if we remember what I said here is that sodium position sodium and this chlorine position, sodium positions are related by this face centering translation. Here, you can see this is what I discussed this, if you apply the face centering translation, this one then sodium positions, you can get it. Same as closing position and they are also interchangeable.

So, what we can do is that whenever in lattice and unit cell contains a common translation which is in this case is face centering translation, both sodium contents of a centering translation, chlorine contents of a centering translation. So, if this kind of a common translation exists in the unit cell then we can factorize we can take a common factor in the structure factor calculation during structure factor calculation.

We can take out a common factor out of this, how to do that I will show so, we will write the same this structure factor F but now, we are taking a common factor and that common factor in case of chlorine, we will do, will not touch the sodium part, we will write the same thing that is e phi i into h + k and + e phi i into k + l + e phi i into l + h, here what we will do for chlorine part? We will take a common factor out here like this h + k + l here.

And this will give us here what will be left is this 1 + e phi i into – h – k + e phi i – h – l + e phi i into – k – l. If I take this common factor out here from this expression so, this is what is left and remember we have already said this e n phi = e – n phi, this is an important relation during when we were discussing about useful relation we said this is how the complex in complex numbers.

This relation is valid power series expression of complex number this relation is valid. So, if we take that relation, what we can just do it here, we can put it back here and what we can get is basically this again this entire term we can take this will become the same. So, we will just remove this. What we will do is that we can in order to save time, we can remove this, we can remove this, we can remove this.

So, then what will it become is basically h + k, h + l and k + l. So, then we can take this part and this thing becomes the same. So that means, we can take this common part we can take it out we write e phi i h + k + e phi i k + l sorry e phi k + l + e phi i l + h, this is the common term and then the rest of the term f Na + f chlorine into this term e phi i and h + e + l.

So, this is exactly the same part as the face center case. So, this part represents to the face centering translation. So, this is what we have discussed during when we were deriving the face centering the structure factor for face centered structure they are the same term appear. So, this is related to the face centering translation. Whereas, this is the new part which is coming because of this special unit cell where 2 different types of atoms are present and both of them are kind of interpenetrating.

So, we are considering the entire unit cell, if I consider the entire unit cell this is the basis part this represent the basis part sodium in the FCC and chlorine in another FCC or sodium and then octahedral void positions chlorine. So that kind of a unit cell is this is represented this is the simple FCC or face centering translation. This part represent FCC translation. Now, how do I solve this thing? This one is known to us that how to solve this one.

So, let us first imagine what will happen, if h k l when we will get no intensive let us first derive that that is easier. So, if we do not get, if we get h k l mixed, we have already seen this in case of an FCC cell. So, if h k l is mixed, this part is 0 ultimately F will also be 0. So, h k l mixed condition we will not get any intensity for that particular plane. For example, we will not get anything from 1 1 0 or we will not get anything from 1 0 0 in that way it is similar.

It is same as normal FCC. So that says that this is basically an FCC unit cell with some other kind of modification. What is that modification? That we have to see and for that this will be another this will add additional conditions in the structure when h k l is unmixed. So that we have to now consider h k l is unmixed in case of normal FCC and mixed, if in case of normal FCC, if it is unmixed we should always get intensity.

In this case, there is an additional condition on top of that for unmixed condition that additional is what we can write the structure factor F equals this part is anyway giving me 4, if you remember, if it is unmixed + now, I have this f Na + f Cl and this additional term e phi i h + k + l. This one is similar to the body centered condition. So, if you remember the bodies entering there, if we get this h + k + l even an odd depending on that.

We are getting some intensity sometimes and sometimes we do not get any intensity in this case that will not happen but additional condition in unmixed, if unmixed condition, if I get h + k + l is this is even then and this is odd 2 conditions I am now considering one is even one is odd. If this is even then the structure factor F will have 4 f Na + f Cl. This is what we have seen in case of BCC that when h + k + l is even this will come out to be + 1 this entire thing will come out to be + 1.

So, this ultimately will be f Na + f Cl whether whereas; if it is odd then this will be 4 into f Na – f Cl. So that means, we will have a modification in intensity depending even, if it is an unmixed one depending on that whether h + k + l even or odd we will have a mixture or will have some modifications in intensity for an initial structure.

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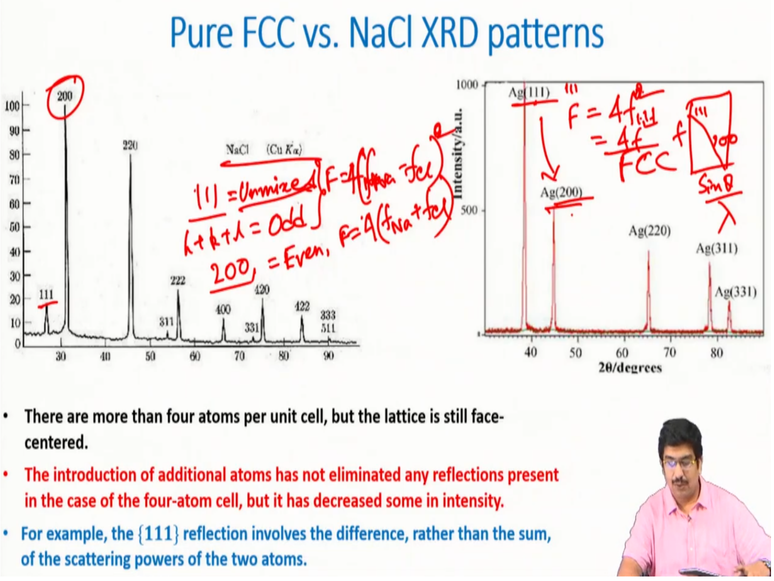

Pure FCC vs. NaCl XRD patterns

- There are more than four atoms per unit cell, but the lattice is still face-centered.
- The introduction of additional atoms has not eliminated any reflections present in the case of the four-atom cell, but it has decreased some in intensity.
- For example, the {111} reflection involves the difference, rather than the sum, of the scattering powers of the two atoms.

So, let us now consider or let us now compare this pure FCC and sodium chloride structure and this will be far more clearer now. So, what we will be taking now, let us say 1 1 1, 1 1 1 reflection. So, 1 1 1 for normal FCC is this one the highest intensity peak first and highest intensity peak for an regular FCC. This is a regular FCC case, regular FCC 1 1 1 is the highest intensity and the first peak.

What will happen in case of an NaCl structure to the 1 1 1? It is an unmixed fine. So, definitely I will get some intensity but again, if I look at this h + k + l condition, this is coming out to be an odd number. So, ultimately for this one I will get F = f Na sorry its 4 will be there, 4 into f Na – f Cl. This is a structure factor for 1 1 1 in case of NaCl whereas, in this condition structure factor for 1 1 1 same 1 1 1 plane structure factor, this is the same type.

So, simply this is 4 f squared, whereas, in this case, this is for this 4 f this 4 Na minus sorry, this will not be there, F = 4 f in this case f = 4 into f Na – f Cl. So, this is the difference. So, definitely the intensity of these 2 will be different or at least the expression is different. But if I consider let us say something like 2 0 0 planes, 2 0 0 in this case again it is an unmixed and h + k + l is here it is even.

So, F in this case will be 4 into f Na + f Cl. And hear the same thing here f Cl will be always the same always 4 f square that here there is no difference, no modification is happening whatever this one of course, the intensity of this 1 1 1 peak and 2 0 0 peak will be changing because the atomic scattering factor of 1 1 1 plane and 2 0 0 plane is different. That is why 1 1 1 is the highest.

If you remember this atomic scattering factor the way atomic scattering factor was changing with sin theta by lambda. So, sin theta by lambda for 1 1 1 peak and this is possibly for 2 0 0 peak that is completely different. That is why 1 1 1 peak in this case will be the highest 2 0 0 peak intensity will be lower for a simple FCC but if we look at the NaCl structure.

Now, 1 1 1 peak will have a lower intensity compared to 2 0 0 peak because in case of 1 1 1 peak, the intensity is f Na – f Cl, whereas, for 2 0 0 peak it is f Na + f Cl. So, this kind of a modification in the intensity will happen because of this additional restriction not only unmixed it has to then we have to see whether it is even or odd, h + k + l is even or odd. And this is the kind of, if you go for complex crystal structure.

This is the kind of additional conditions which will come which will modify the intensity and sometimes which will remove certain intensity from certain planes at all. So, this is NaCl case you can go on and derive such expression for many other crystal structures. So, we will be stopping with our discussion about structure factor here and we will be moving towards some other kinds of factors.

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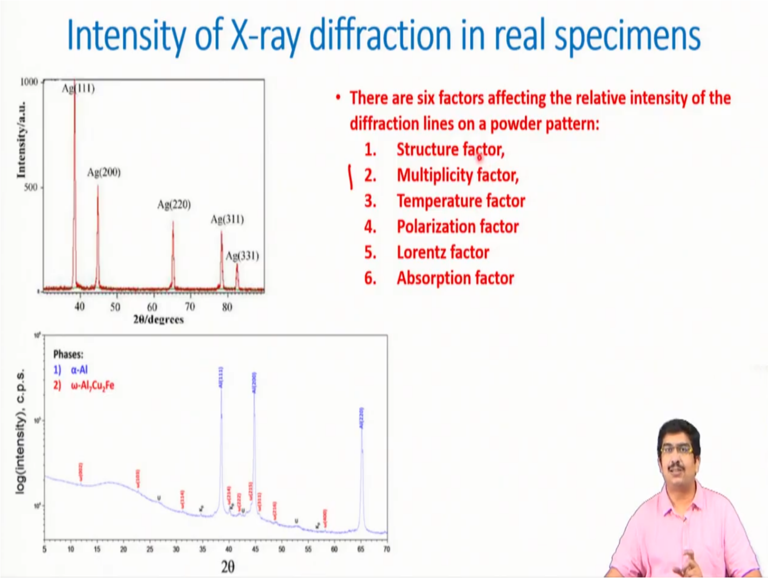

Intensity of X-ray diffraction in real specimens

- There are six factors affecting the relative intensity of the diffraction lines on a powder pattern:
  1. Structure factor,
  2. Multiplicity factor,
  3. Temperature factor
  4. Polarization factor
  5. Lorentz factor
  6. Absorption factor

But for that the first thing we will be seeing is basically the intensity of a real specimen in real X-ray diffraction specimen So, if you see the normal FCC structure, so, this is a normal FCC structure, where 1 1 1 claim should have the highest intensity. If it is just a regular FCC, I am not even considering NaCl or any kind of complex crystal structure and just pure and simple FCC single element FCC structure.

So, 1 1 1 should be the highest peak 2 0 0 should be the next highest peak and so on and so forth. But if you look at real specimen, this is this one is for an example of FCC aluminum, aluminum alloy, basic aluminum copper type alloy. So, in aluminum copper type alloy which is a real specimen, not even a powdered specimen, this is a powder specimen this one is and both of them are taken at room temperature this is silver powder.

Whereas, this one is aluminum solid specimen and you can see that 1 1 1 intensity is almost comparable to the 2 0 0 intensity here and even, if you look at 2 2 0 that intensity also is not that different and what another thing you can notice is the intensity decrease in the background that also is very much apparent here in case of a real specimen. So that means, basically what this means is the intensity there are much more factor there are many factors other than the structure factor or atomic scattering factor and so, on.

Other than those factor there are many other factors which are responsible for modifying the intensity of a real X-ray diffraction pattern. So, there are basically 6 factors in general, if we consider all different types of X-ray diffraction patterns. So, there are at least 6 different factors which are responsible for modifying or for determining the intensity of any real diffraction pattern.

So, this is structure factor we have already discussed about that and in structure factor basically contents or structure factor basically covers the atomic scattering factor on all of these things. So, structure factor is of course, one of them, multiplicity factor this is also another big very important factor and which is related to the crystal structure or atomic arrangement within the unit cells, this structure factor and multiplicity factors.

These 2 factors are crystalline that means, related to the atomic arrangement of any within any at the unit cell. Third one is a temperature factor purely the atomic vibration because of the temperature related to that we will discuss about this. Polarization factor we have already discussed, if you remember that intensity when we were discussing about the intensity coming out of for entire atom.

And there electrons the intensity of an electron at certain point i p and they are i p = i 0 into 1 + cos square 2 theta by 2 and we said that 1 + cos square to theta by 2 that factor is called Polarization factor which was simply entering the diffracted beam intensity because the beam is not polarized, if it is polarized then this factor on there.

That is the Polarization factor which is related to the geometry of the diffraction or the related to the beam itself. Similarly, there is another factor which is called Lorentz factor we will not discuss into that. Lorentz factor is again a geometrical factor which enters because of the geometry of this entire detection system. The position of the detector and all will not discuss together.

Lorentz and Polarization factor basically, many times they are clubbed together and called Lorentz Polarization factor. We will not discuss absorption factor is related to the X-ray absorption we will briefly discuss about this but not in any detail. Basically, structure factor multiplicity factor these are very important temperature factor also.

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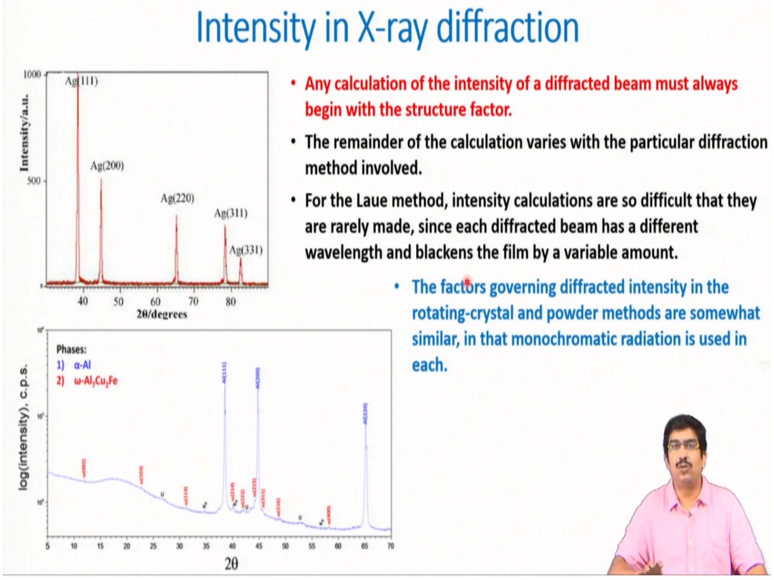

Intensity in X-ray diffraction

- Any calculation of the intensity of a diffracted beam must always begin with the structure factor.
- The remainder of the calculation varies with the particular diffraction method involved.
- For the Laue method, intensity calculations are so difficult that they are rarely made, since each diffracted beam has a different wavelength and blackens the film by a variable amount.
- The factors governing diffracted intensity in the rotating-crystal and powder methods are somewhat similar, in that monochromatic radiation is used in each.

So, when we calculate the intensity of a diffracted beam, we should always start with the structure factor. If structure factor is saying that certain intensity will not be there, it will not be there at all. So, structure factor is out of all these factors for a crystalline material at least out of all these factors structure factor is the most important factor and structure factor is primarily responsible for the intensity from any diffracted beam from any crystallographic plane.

If that structure factor says it is a forbidden reflection that will not be affected by any other factor. Only if structure factors allows permits the diffracted beam to have certain intensity from certain crystallographic plane then only the other factors will modify the intensity of this plane. So that is most important is the structure factor in, if you want to calculate, if you want to analyze the intensity of an extra diffracted beam.

And for and this intensity again will decrease on specific X-ray diffraction method for example, Laue diffraction, there the calculation of the intensity of the diffracted beam is very very difficult. And it also depends on the sensitivity of the film over which this X-ray diffraction pattern is calculated. So, we will not go into there, mostly at the present day we most important or most popular diffraction X-ray diffraction method is border diffraction method or solid sample diffraction method.

And we will be just discussing about that and we will be discussing about those factors which are where monochromatic radiation is used and we are getting the intensity, X-ray intensity in a detector in a real detector.

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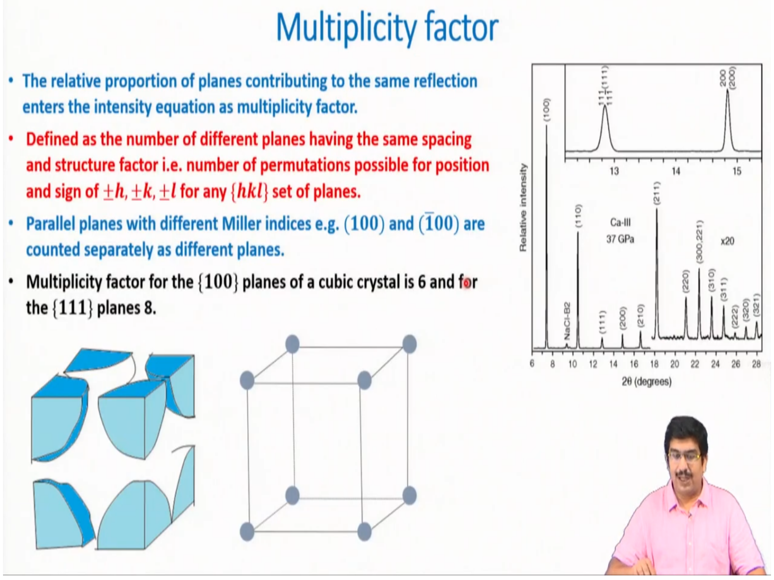

Multiplicity factor

- The relative proportion of planes contributing to the same reflection enters the intensity equation as multiplicity factor.
- Defined as the number of different planes having the same spacing and structure factor i.e. number of permutations possible for position and sign of $\pm h, \pm k, \pm l$ for any $\{hkl\}$ set of planes.
- Parallel planes with different Miller indices e.g. (100) and $(\bar{1}00)$ are counted separately as different planes.
- Multiplicity factor for the $\{100\}$ planes of a cubic crystal is 6 and for the $\{111\}$ planes 8.

There we will see how the different factors will modify the intensity of this. The first of all is basically the multiplicity factor as I said, this is related to the atomic arrangement, this is basically related to the multiplicity of atomic planes but this we will be covering in the next class along with the temperature. Thank you.