Techniques of Materials Characterization
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Lecture - 55
Intensity of diffracted beam (Continued)

Welcome everyone to this NPTEL online certification course on Techniques of Materials Characterization. We are in module 11, we are still continuing with X-ray diffraction and in the lecture 5 we will be covering again intensity of diffracted beam some other factors of how they influence the intensities. Until up to now, we have discussed about mainly one factor which determines the intensity that is structure factor.

And we have derived an expression of structure factor from by taking right from an how extra scattering happens from an individual electron and then how that sums up for an atom and then all the atoms which are part of an unit cell. So, from there we have derived an expression of structure factor and then we have derived the structure factor for various type of crystal structures like simple, base centered, body centered, the face centered and more complex one like sodium chloride we did that in the last class.

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CONCEPTS COVERED

- Multiplicity factor
- Temperature factor
- Absorption factor

And now, we will be moving forward and we will be trying to talk about some other effects, which are responsible for modifying the intensity of X-ray diffraction beam. So, one of them is multiplicity factor and temperature factor this is what we will try to cover here absorption factor possibly we will discuss in the next lecture.

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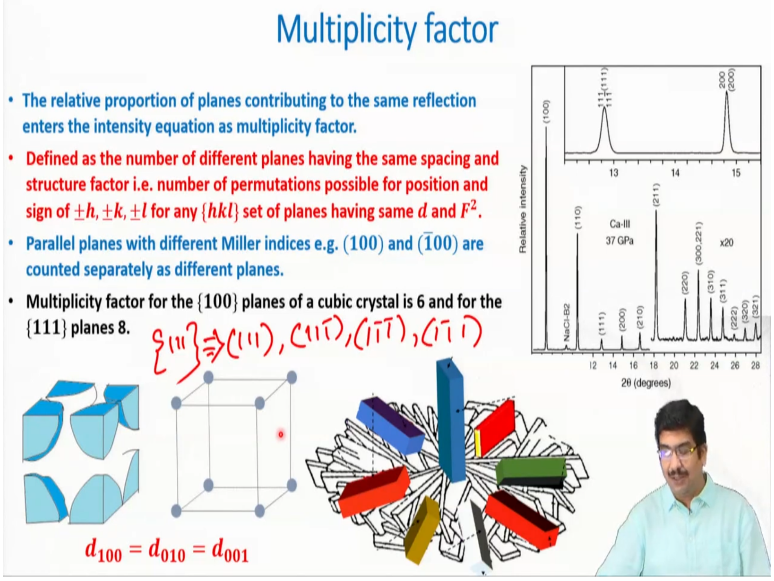

Multiplicity factor

- 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 having same d and F^2.
- 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.

$\{111\} \Rightarrow (111), (11\bar{1}), (1\bar{1}\bar{1}), (\bar{1}\bar{1}1)$

$d_{100} = d_{010} = d_{001}$

So, the first one is multiplicity factor. So, what does multiplicity factor does, this do? So, multiplicity factor is basically responsible or it is related to the multiplicity of various crystallographic planes in a crystalline material. So, for example, if we take the simple cubic system, simple cubic, just a simple cubic system, unit cell is shown here. So, in this simple cubic, if we consider something like 1 0 0 type plane.

So, I believe everyone knows about the type of planes and a specific planes the difference between a type of planes and specific planes. Whereas, the curly brackets basically h k l in a curly bracket means, the type of plates like combination of many plates which are possible with a permutation combination of this number, especially for cubic system.

I am talking, about or I am not talking about other complex systems. And when there is a first bracket instead of a curly bracket, there is a straight bracket like this that means a specific plane. So, it is basically the multiplicity of any type of plane or class of plane the multiplicity number how many permutation combinations you can make that also affects the intensity of the diffracted beam.

The question is how? So, we take a simple example, we take something like 1 0 0 type plane of a simple cubic structure. So, 1 0 0 type planes means, this side plane, so, there are 6 such side planes possible from this cube, this simple cubic unit cell. So, there are 6 such side planes possible and since it is a cubic system all of this everything a b c all lattice parameters are the same and angles a 90 degree.

What happens is that if I consider this family of planes this 6 side planes and 6 side planes means, I can consider them as either 1 0 0 and bar 1 0 0 basically. And then 0 1 0 and 0 0 1 this 3 types the basically this means, these 3 sides, sets of sides, these 2 planes, these 2 planes and these 2 planes. If I consider like this then what I will see is that they will be basically having the same d value, the distance because everything is same here.

So, the distance between these 2 planes, these 2 planes and these 2 planes is exactly the same, interplanar spacing is basically the same. So, they will be satisfying the Bragg's condition exactly at the same 2 theta position. If I take now, the extra diffraction profile here from the simple cubic structure, I will see that I will get only one peak corresponding to this 1 0 0 planes, 1 0 0 type of planes or 1 0 0 family of planes.

I will get one single peak out of them because they will be satisfying they are having exactly same d values. So, if lambda remains constant d remains constant then sin 2 theta will also be constant that means, they will be forming a diffracted beam exactly at the same angle, meaning all the diffracted beams coming out from all 3 sets of planes, they will be sort of coincided with each other.

So, ultimately I will be getting a peak which is sort of which is a combination of all 6 planes. The beam diffracted beam coming out of all these 6 planes will coincide, I can imagine that they will be summed up and they will be forming this one single peak belonging to 1 0 0. Tie family of planes that is fine. Now, if I consider instead of 1 0 0 I consider something like 1 1 1 plane. So, 1 1 1 plane will can have, if I just have to write it, if I write then it will possibly be even more clear.

If I consider something like 1 1 1 plane, family of planes and this here I can write this will be having something like 1 1 1, this will have 1 1 bar 1 and then I can have 1 bar 1 bar 1 and 1 bar 1 1. These 4 type of planes again this means these planes and they are opposite just putting a bar on top of that so, opposite. So, these 2 sets up 1 1 1 planes similarly, will be forming again they are the d spacing is exactly the same, it is a simple cubic structure.

So, their deep spacing is exactly the same and they will be again forming the peak in the same position same 2 theta value. Now, the point is that in a 1 0 0 type plane, I can make this combination, I can have 6 such planes, 6 side planes. Whereas, in 1 1 1 type plane I can have 8 such planes. So, 4 here and reverse, opposite 4 opposite planes. So, there are 8 such planes in possible in case of 1 1 1 type of family of planes whereas there are 6 such possible planes in case of 1 0 0 type of plane.

That means, the relative proportion of 1 1 1 type plane is higher than 1 0 0 type plane. So, if I consider that each of these planes are giving some amount of intensity, the way we calculated it for, if you remember the structure factors and the way we calculated the intensity from one single atom. So, if I just imagine that then that means 8 1 1 1 type of planes are giving me an intensity versus 6 1 0 0 type planes giving me an intensity.

So, ideally the 1 1 1 type plane should have a higher intensity. if I just imagine that all the atoms are giving the same intensity of the diffracted beam, scattered beam. Then the 1 1 1 planes should have a higher intensity compared to 1 0 0 planes theoretically. It is not happening here, not shown here because of other factors but ideally that is what it should do. Now, this is called.

So, how do I take care of this multiplicity of the number of planes possible in a family of planes? So, that factor is known as the multiplicity factor and the way we can define it, it is basically I will let me bring that laser point again. So, it is a relative proportion of planes that is contributing to the same reflection. So, relative proportion 1 0 0 type of planes all of them contributing to the same reflection same place.

They are giving the satisfying the diffraction condition and the for the same 2 theta value. So, this number the relative proportion that is known as multiplicity factor and that goes in the final intensity of the scattered beam. So, it should be multiplied with its multiplicity factor and it is the way it is defined is basically the number of different planes possible in that family of planes with having the same spacing and structure factor.

That means, the number of permutations basically the number of planes or number of permutations possible for the position and sin up this plus minus h plus minus k plus minus l in a h k l plane. So, again, if I write it down already it is there anything already 1 1 1 is there, you can just imagine that 1 1 1 and bar 1 bar 1 bar 1. So, 11 bar 1, bar 1 bar 11, so, like this 1.

So, here this plane opposite to it will be bar 1, 1 1 and opposite to this will be 1 bar 1, 1, bar 1. So, this 8 plates, so, that is the number that is a multiplicity factor. And in this case of course, the multiplicity when we calculate the multiplicity factor remember one thing that parallel planes with different Miller indices. So, these 2 are parallel planes, if we consider these 2 as 2 parallel planes and these 2, if I consider them something like 1 0 0 type of plane.

I have to take 1 0 0 and bar 1, 0 0 one of them will be 1 0 0 plane one of them will be bar 1, 0 0. And it is very related because you can shift the origin. So, these 2 should be taken as 2 different planes. So, ultimately the multiplicity factor for 1 0 0 type of plane 1 0 0 family of planes will be 6 for cubic crystal. At least, will be 6 and for 1 1 1 type plane for the cubic crystal it will be 8.

So, that is the multiplicity factor ultimately the intensity I get for 1 1 1 plane should be multiplied with 8 whereas, the intensity final intensity I get from 1 0 0 plane should be multiplied with 6.

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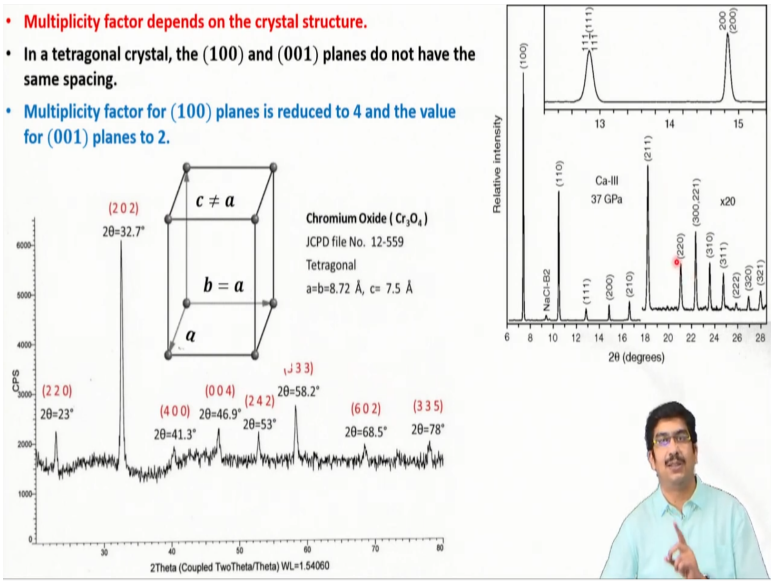

- Multiplicity factor depends on the crystal structure.
- In a tetragonal crystal, the (100) and (001) planes do not have the same spacing.
- Multiplicity factor for (100) planes is reduced to 4 and the value for (001) planes to 2.

That is a multiplicity factor that goes here. Now, the important point is that multiplicity factor basically depends on the crystal structure. What kind of a crystal structure and why is it so? That is basically, if we consider the tetragonal crystal. So, in a cubic crystal, we have seen the multiplicity of 1 0 0 family of plane is 6. What happens for a tetragonal case unit cell is that? In tetragonal we know this a and b is same but c is not equal to a or b.

So, c axis is a different, it is of different length. So, what happens is this planes this 2, this top one and bottom one. These planes the interplanar spacing will be different from 4 side planes, these 4. So, this plane and this plane and this backplane and front plane this will have the same interplanar spacing which is equal to a. Whereas, this planes the top and bottom plane will have an interplanar spacing of c which is not equal to a.

So, that means, in case of a tetragonal crystal 1 0 0 and 0 0 1 planes, they do not have same spacing. So, I should consider them separately and the multiplicity factor for 1 0 0 planes the 4 side planes the 1 0 0 planes will be 4 whereas, the multiplicity for 0 0 1 plane which is different than 1 0 0 plane will be 2. So, here I have to consider this is a different case from simple cubic, here I have to consider them separately.

And if you look at this diffraction pattern here, if you see the diffraction pattern here then you will see that we are getting 2 2 0 and 0 2 0 2. So, basically both of them are from 2 2 0 family of planes they are counted as 2 separate planes here. You, if you can see here the 2 2 0 for a simple cubic system 2 2 0 type of plane is only 1, there is no difference between 2 2 0 and 2 0 2.

These are not 2 different planes or same family a plane for a cubic system. But for a tetragonal system 2 2 0 and 2 0 2 are 2 separate planes and they appear separately in the X-ray diffraction pattern that is why when we calculate the intensity of these 2 we have to take them to separate here. 2 2 0 planes we can calculate their multiplicity only once. Here the multiplicity of 2 2 0 and 2 0 2 planes will be completely different.

That is the effect of multiplicity factor for various different crystal systems and that makes the intensity calculation even more difficult. Because still now, we are considering only cubic system which is very symmetric, tetragonal, more symmetric much more like compared to cubic less symmetric but compared to other crystal system it is much more symmetric.

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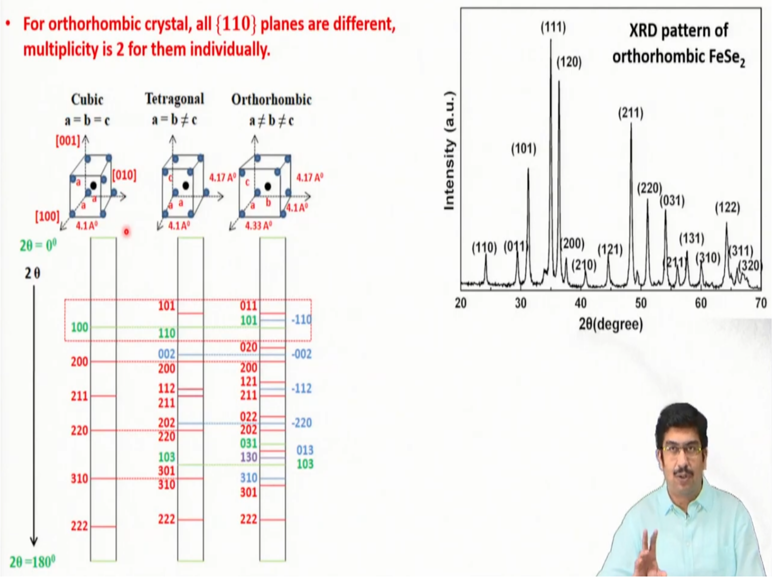

- For orthorhombic crystal, all {110} planes are different, multiplicity is 2 for them individually.

If you go to orthorhombic system it is becomes even more complicated. For example, orthogonal system all 1 1 0 type planes are different. So, even cubic system 1 1 0, there are only 2 types of 1 1 0 planes. So, 2 2 0 and 2 0 2 type in case of orthorhombic crystal, all 1 1 0 planes are different and that is why they will be having multiplicity factor of 2. So, any plane, unique plane will have multiplicity factor of 2 because that plane and the reverse of it.

So, two 1 1 0 planes for orthorhombic crystal, all of them are different and all of them will have different crystal or different multiplicity factor. And that is what is shown here that if you consider body centered cubic versus body centered tetragonal versus body centered orthorhombic systems then 1 0 0 plane itself for cubic system 1 0 0 type of planes are all same, all 6 are same.

Whereas for tetragonal system again you have completely different type of 1 0 1 and 1 1 0 planes. And then if you go to orthorhombic you have all 3 different type of all 1 0 0 planes, they are different, completely different. If you go to 2 0 0, again, here in case of cubic system all of this family of planes are unit or means all of them are the same, all the planes are same.

The multiplicity factor is 1 unit value they will give you only 1 single peak whereas, if you go to tetragonal, if you go to orthorhombic you will be getting different peaks for them with different multiplicity factors. So, if you see this orthorhombic crystal structure here for iron selenide then you will see 1 1 0 0 1 1 1 0 1 all of them for cubic all of them is 1 1 0 type family of plane.

But for an orthorhombic system, you are getting them completely separately 1 1 0 0 1 1 1 0 1. All of them are giving separate crystalline peak because they separate planes there. Obviously, the multiplicity factor is also different in this case. All the multiplicity factor for each of them is 2 in this case. So, that is the effect of multiplicity factor in determining the intensity, absolute intensity of various planes.

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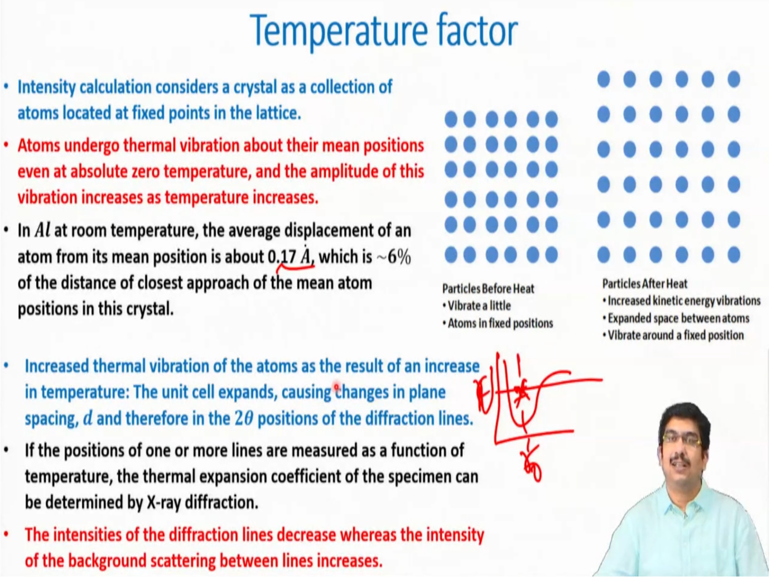

Temperature factor

- Intensity calculation considers a crystal as a collection of atoms located at fixed points in the lattice.
- Atoms undergo thermal vibration about their mean positions even at absolute zero temperature, and the amplitude of this vibration increases as temperature increases.
- In Al at room temperature, the average displacement of an atom from its mean position is about 0.17 $\dot{A}$, which is ~6% of the distance of closest approach of the mean atom positions in this crystal.

Particles Before Heat
- Vibrate a little
- Atoms in fixed positions

Particles After Heat
- Increased kinetic energy vibrations
- Expanded space between atoms
- Vibrate around a fixed position

- Increased thermal vibration of the atoms as the result of an increase in temperature: The unit cell expands, causing changes in plane spacing, d and therefore in the 2θ positions of the diffraction lines.
- If the positions of one or more lines are measured as a function of temperature, the thermal expansion coefficient of the specimen can be determined by X-ray diffraction.
- The intensities of the diffraction lines decrease whereas the intensity of the background scattering between lines increases.

So, the next factor that we need to consider is called the temperature factor. Now, temperature factor, what is the effect? As the name suggests it is something to do with the temperature itself. So, when we calculate the intensity basically when we just simply calculate the let us say structure factor when we started with an electron intensity of an scattered X-ray from an electron then we went to the atom.

Then we went to the unit cell, one thing we sort of assume that this intensity calculation we did not consider crystal or rather we consider crystal is a collection of atoms which are located at fixed points in the lattice. That means, they have no movement, no vibration. So, this is what the condition possibly we have assumed that at any given point of time all of them are situated at a fixed distance from each other.

There is no moment they are just touching along certain direction, they are touching and they are fixed. They are rigid bodies which are fixed in position. But, we know that atoms undergo thermal vibration about the mean position. So, there is a vibration and that we discussed about the during phonon scattering and all. So, atoms move about their mean position even at an absolute 0 temperature absolute 0 temperature it is very minute.

But still it is there. So, even, if you increase the temperature of course, this amplitude of this movement, this motion, the thermal vibration, the amplitude of this increases as the temperature increases and if we think that it is something at a higher temperature at any given point of time this because of thermal vibration. The distance between this atoms are continuously changing it is not a fixed one, continuously there is a movement and the distance between the atoms are continuously changing.

Now, the amount of this thermal vibration is not something you can neglect so easily. For example, if you take aluminum at room temperature the average displacement about its for an atom about its mean position is around 0.17 angstrom which is almost 6% of the equilibrium distance between the atoms closest approach of the mean atomic position. Basically that is the equilibrium distance.

If you remember or, if you have saw this that this what are we talking about is this. Basically, what we are talking about is this equilibrium distance of separation where force, if we can write the force. This is the equilibrium distance. So, this called interatomic potential versus or this is interatomic potential I am sorry, this is not force this is interatomic potential. So, interatomic potential versus distance curve.

So, this is the mean position and this distance is almost 6% the thermal at room temperature the atomic vibration is almost 6% of this into this equilibrium distance here. That much of thermal vibration that much change in the atomic position can happen just by increasing the temperature all the way from absolute 0 to room temperature 273 Kelvin. So, now, this increased or this thermal vibration this amount, this is almost similar.

This amount that we are seeing here this 0.17 angstroms. This distance is almost the distance of separation between electrons within the atom itself. So, that means, if I assume that entire atom is vibrating and this much of distance is their covering that will impact the intensity of the diffracted beam because this in this situation what we can just to understand in this situation, the constructive interference that is basically finally forming the diffracted beam.

And that is what is separating the diffracted beam from a scattered beam, regular scattered beam the diffracted beam a special phenomena where constructive interference is involved.
There will be a certain problem or there will not be a complete constructive interference just because of this moment. This atomic moment which is of the order that can be that is enough

to sort of modify or that is enough to affect this entire phenomena of constructive interference.

So, this thermal vibration, let us see how this thermal vibration can affect the intensity of the diffracted beam? The first thing it can do does this thermal vibration is it can expand the unit cell. So, if we imagine that this is one of the atomic planes we are seeing here. We can imagine that due to thermal vibration now, the atoms are sort of, further apart from each other.

And the unit cell has expanded that means, if the unit cell is expanded that means, we are sort of we are getting now, a change in the lattice spacing, we are getting a change in the interplanar spacing and if we have a change in the interplanar spacing from the relation again lambda = 2 d sin theta. We are having a change in the d value obviously, lambda is a constant for any **(()) (20:30)** X-ray.

D value is changing we will be getting diffraction at a different sin theta value. So, we will not be getting diffraction condition satisfied at exact Bragg's condition we will be getting it in different other than non Bragg's angle other angles there will be an diffraction condition satisfied just because the unit cell is now, expanded and that means, this d value is changed. So, this is first effect that this thermal vibration can cause.

Now, if we can measure this peak width somehow, if we can measure this position of diffraction this diffraction lines how much shift it is showing in terms of 2 theta in sin 2 theta how much this shift is happening due to the increase in temperature that means, due to the change in d value due to thermal vibration the change in d value and how much 2 theta? How much change in sin 2 theta is happening? If we somehow with temperature, if we somehow measure it.

That can help us to identify the thermal expansion coefficient of the specimen just from an X-ray diffraction technique. We can find out the thermal expansion coefficient of the specimen by measuring the peak positions with respect to the temperature that is possible and that measurement is very, very accurate, if the X-ray diffraction has no other issues involved with it.

The issues that we will be discussing maybe in the next module, if those issues can be solved in such a way, this is one very nice method to find out the thermal expansion coefficient of any material from X-ray diffraction. But I am not going into details of that fine. So, that is the first effect that shift in the 2 theta position peak will be shifted in the 2 theta position. Even more prominent effect that this temperature the thermal vibration will produce is basically the intensity of the diffraction intensity of the peak will decrease.

Whereas, the intensity of the background will increase, background in the diffraction but the entire other scattering angle the background that intensity will increase. The peak intensity will decrease and the background intensity will increase, if we increase that temperature.

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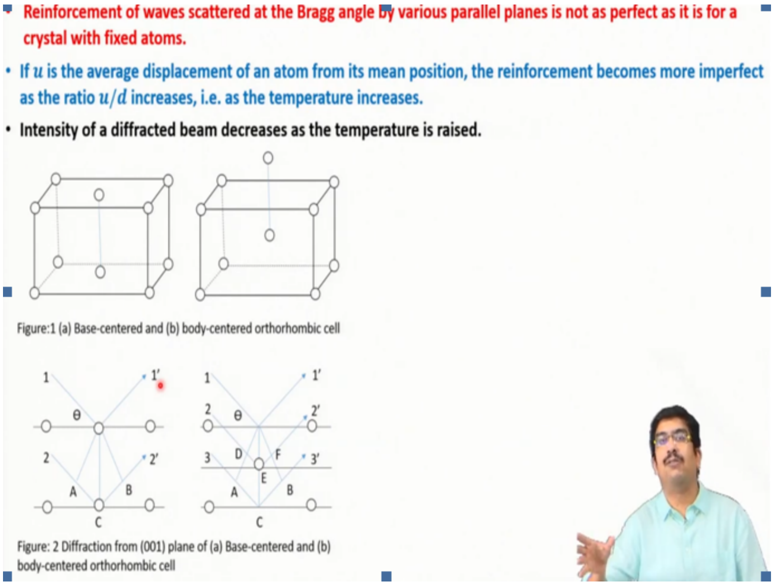

- Reinforcement of waves scattered at the Bragg angle by various parallel planes is not as perfect as it is for a crystal with fixed atoms.
- If u is the average displacement of an atom from its mean position, the reinforcement becomes more imperfect as the ratio u/d increases, i.e. as the temperature increases.
- Intensity of a diffracted beam decreases as the temperature is raised.

Figure:1 (a) Base-centered and (b) body-centered orthorhombic cell

Figure: 2 Diffraction from (001) plane of (a) Base-centered and (b) body-centered orthorhombic cell

Now, why this is happening that is what we have to understand. What we said is that due to the temperature. Of course, now this atoms we go back to this geometric construction for Bragg's Law determination we go back there for base centered body centered we know. What now? We are imagining that when we were seeing this entire construction.

We were imagining that all the atoms are fixed in their own position that is why we were considering for base centered 1 0 0 planes, we were able to consider all of the atoms lying on the same plane and for this base center body centered consideration we were able to imagine a extra plane in the middle. Now, what is happening here is because of the thermal vibration not, may not all the atoms may not lie on the same plane.

So, this atoms may not may be lying this atom perhaps possibly lying a little below then this this one is possibly a little above then this because of this thermal vibration around this position, same thing for this atoms all of them. Now, what will this make or what the effect this will have is that this entire constructive interference you know the constructive interference needs, the path difference has to be an equal integral multiple of the wavelength.

So, this entire geometric condition but because of this thermal movement because all of this atoms are now, having little movement in their atomic position. So, this distance will be also changing, let us imagine that this distance is basically changing due to that increase in the temperature. So, I am increasing the temperature and this distance between these 2 atoms these 2 atomic planes are changing.

So, that means the constructive interference this path difference will not be an exact integral multiple of the wavelength of the incoming X-ray and that is why we will not be getting an exact constructive interference from parallel set of planes or that or in other words, the reinforcement of this waves that is scattered that exact Bragg angle from parallel planes this will not be as perfect as it is for crystal with fixed atom.

When we imagine that this d value is changing, basically, the reinforcement will not be that perfect from parallel set of planes. So and obviously that will affect the final intensity because only in the event of constructive interference, extreme constructive interference we will be getting highest intensity, if anything less than this constructive interference, if any partial interference happens then the intensity will automatically decrease.

So, now, if we imagine that this thermal vibration due to this thermal vibration, the average displacement of atoms from its mean position is something like u then this reinforcement of this raise from 2 different parallel planes. This reinforcement will become more imperfect, as the ratio u by d decreases or as the ratio u by d increases that means, if this displacement around the mean position.

If this increases with respect to the d, the atomic position then this imperfection will also the reinforcement will be less and less perfect. That means, we will be moving away from a perfect constructive interference of course, what it means is that the intensity as I said the highest intensity is obtained when there is a perfect constructive interference. Now, we are moving away from the perfect that perfect constructive interference case.

So, as the temperature increases that means, the ratio u by d, the temperature increases means, u increases even, if d is constant temperature increases means u is increasing and that means now the intensity of the we are going to more and more imperfect situation. The intensity of the diffracted beam will also decrease that means, if temperature increases intensity of diffracted beam also decreases even, if we get the same d value I am considering.

So, earlier we were just considering the effect of d effect of d is still there. The increase the effect of increasing d is reflected in the shift of the peak in sin 2 theta access the peak will shift. But now, we are considering the movement itself the vibration the atomic the average displacement it has about it means position. Because of that is temperature is increasing u is increasing d remains constant.

We are getting we are moving away from an exact constructive interference case, the intensity is decreasing that is the first effect.

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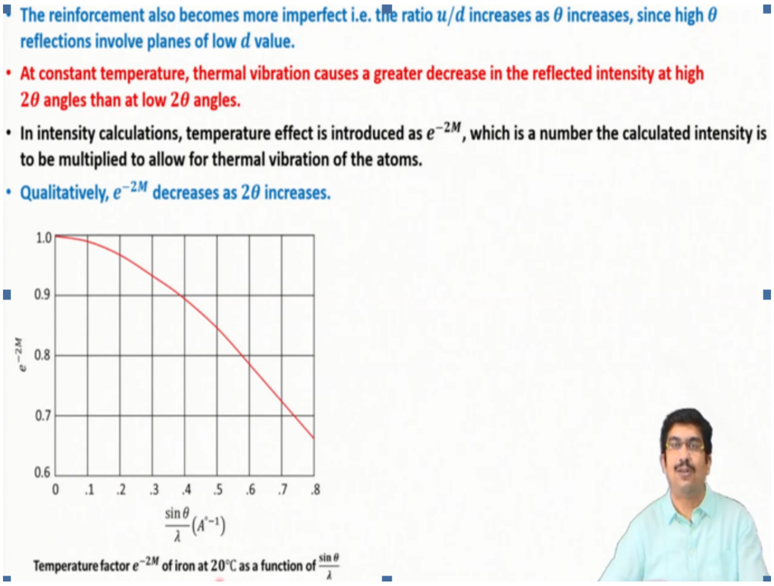

- The reinforcement also becomes more imperfect i.e. the ratio u/d increases as θ increases, since high θ reflections involve planes of low d value.
- At constant temperature, thermal vibration causes a greater decrease in the reflected intensity at high 2θ angles than at low 2θ angles.
- In intensity calculations, temperature effect is introduced as e^{-2M}, which is a number the calculated intensity is to be multiplied to allow for thermal vibration of the atoms.
- Qualitatively, e^{-2M} decreases as 2θ increases.

Temperature factor e^{-2M} of iron at 20°C as a function of $\frac{\sin\theta}{\lambda}$

The second effect that it can have is basically same thing, if we are reinforcement will be becoming more and more imperfect or less perfect, if this ratio u by d increases. Now, even, if the same temperature at a constant temperature same temperature let us imagine that u is constant as theta increases. That means, as we are moving towards higher and higher diffraction angle sin 2 theta we are moving from something like a forward diffraction to backward diffraction.

So, if the sin 2 theta is increasing theta increasing then this d value will decrease that because high 2 theta involves. So, the reflections diffraction for low d values will increase will be more at high 2 theta. So, this comes basically from the same relation lambda = 2 d sin theta. So, d and sin theta is inversely proportional, for lower d value planes which are much, much closer or high index planes.

Basically high index planes which are much closer to each other for them the diffraction occurs at a much higher 2 theta value. So, those planes for them this ratio again u by d will automatically increases. So, at a given at a constant temperature u by d increases for higher 2 theta. So, as the theta value increases, the diffraction angle is increasing again we are getting higher u by d but this time because of the d, d increases and we are getting d decreases.

We are getting an increase in u by d as theta increases that also will be affecting the intensity. So, even at a constant temperature thermal vibration will cause a greater decrease in the intensity of the peak at high 2 theta values then at a low 2 theta value. So, this both the things so, increasing temperature itself will decrease the intensity because u will increase and that decrease in intensity will be more prominent at higher to theta values.

Those peaks which are giving for those low index planes or high index planes which are having low d value. For them this decrease in intensity due to increase in temperature will be much more prominent. So, ultimately all those effects are combined into one parameter which is called the temperature factor and expressed as e by – e raised to the power – 2 M. I am not going how it is derived? And all which is a number that is by which the calculated intensity is to be multiplied.

So, that we can finally get the diffracted intensity with temperature correction. And this e by 2 M as we just now, discuss that it decreases as 2 theta increases. So, highest is basically at 0, where it is 1 that means the intensity the temperature effect is lowest at there. And anywhere we go at a higher 2 theta value basically, going high 2 theta values means, the way it is impacting is sin theta by lambda.

This we have already discussed in atomic scattering factor. So, I am not going here. So, basically sin theta by lambda, if we sin theta by lambda increases, this factor basically decreases, decreases from 1. So, it becomes a fraction. So, if we multiply the diffracted intensity with something like this and compared to versus something like this. Obviously, the intensity will also decrease the intensity will be lower when we are going to higher 2 theta value.

So, that is the relationship and that is what the temperature factor all about. So, more about the temperature factor will be discussing in the next class and also we will be discussing about the absorption factor in the next class. Bye