X-Ray Crystallography
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Lecture - 20
Ordered Disordered Transformation

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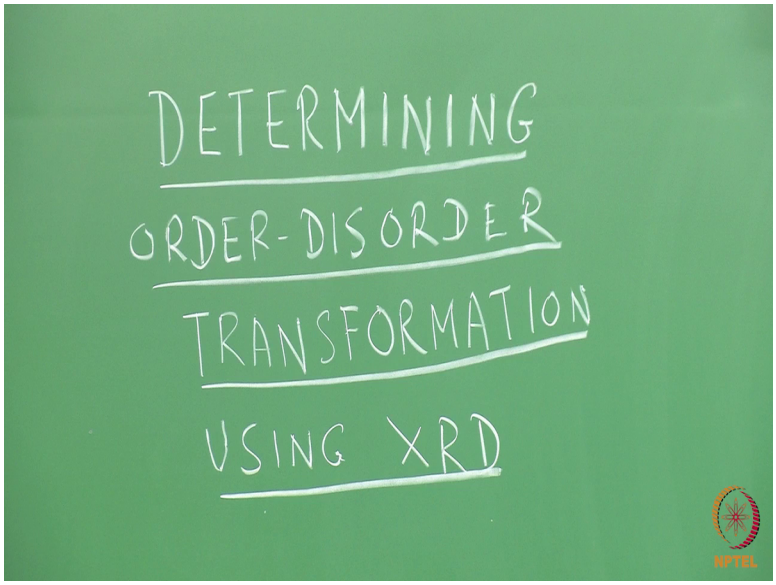

In this lecture I will explain how using X-ray diffraction order disorder transformation can be determined in a material say for example, we have a material Cu Zn.

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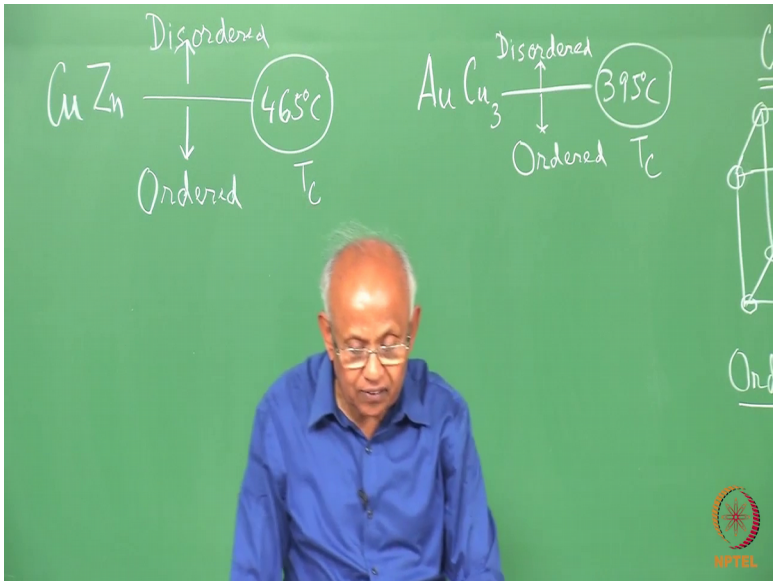

Now, at a temperature below about 465 Cu Zn compound exist in the what is known as the ordered condition above 465 Cu Zn exists in what is known as disordered condition there is a quite a few cases like that I will talk about second compound say Au Cu 3 now above a temperature of say 395 degree centigrade the material exists in a disordered condition where as bellow the temperature of 395 degree centigrade Au Cu 3 exists in what is known as the ordered condition.

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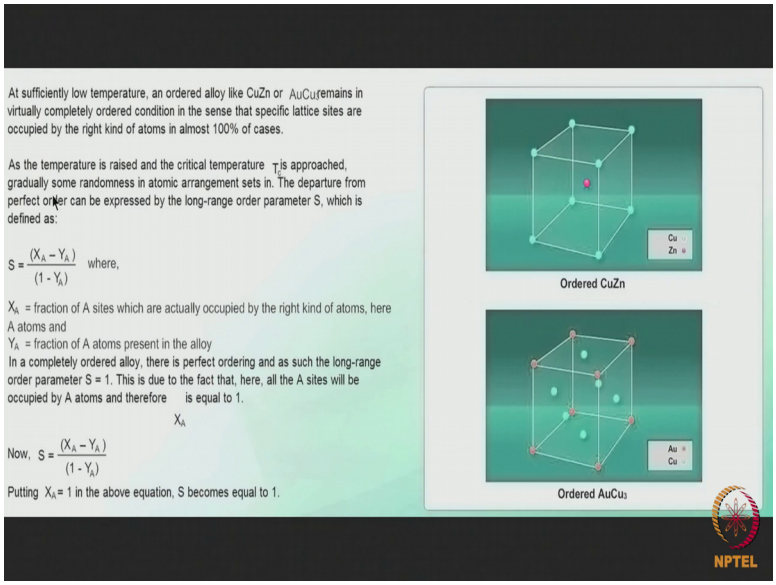

Now, what is this transformation ordering or disordering all about now at sufficiently low temperature we find an ordered alloy like Cu Zn or Au Cu 3 remain in virtually complete order condition in the sense that specific lattice sides are occupied by the right kind of atom in almost hundred percent of cases now let us take the case of Cu Zn in Cu Zn the unit cell is such is a cubic unit cell and the 8 corner positions of the unit cell are occupied by copper atoms and the body centred position is occupied by a gold atom I am sorry by a copper atom by copper atom.

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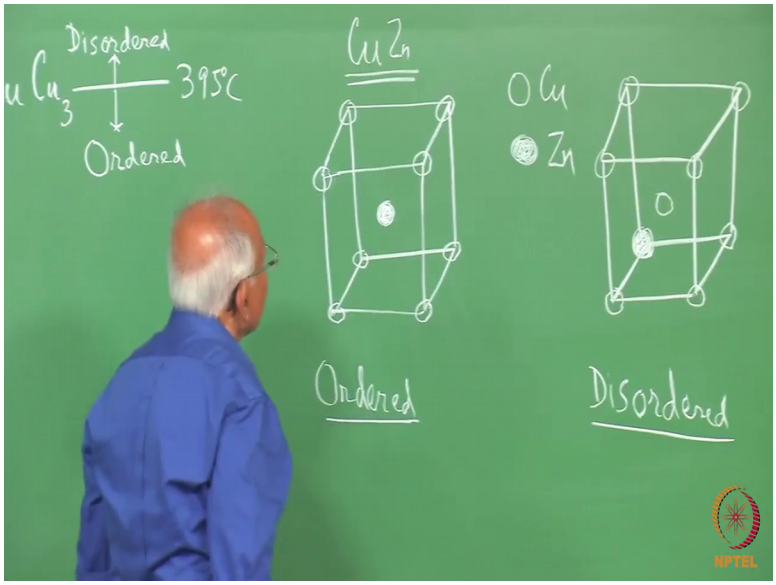

So, in Cu Zn in Cu Zn at low temperature when we say that it is in the ordered condition then the 8 corner locations are occupied by copper atoms and the body centred location is occupied by a gold atom. So, these are the copper atoms at the 8 corners of Cu Zn. So, these are the copper atoms whereas the one at the body centred position is a zinc atom.

So, this is the situation like in Cu Zn below a temperature of 465 degrees centigrade we say that the material is in the ordered condition what it means it means that below 465 centigrade if you look at the lattice of Cu Zn. And you concentrate on a large number of cells in every unit cell you will find that the corner positions will be occupied by copper atoms and the body centred position will be occupied by zinc atoms whichever unit cell you take from the lattice you will find that this will be the situation. That means, copper atoms will occupy the corner positions of the unit cells zinc atom will occupy the body centred position in the unit cell. So, we say that the material is in a completely ordered state now when we take Cu Zn above 465 degree centigrade what happens then.

So, what happens when we take a piece of Cu Zn to a temperature above 465 c then if we look at the different unit cells in the lattice in some we may find out of 8 corner locations seven may be occupied by copper and one may be occupied by zinc and another copper would be at the body centred position in another unit cell we have had a situation that we

have all the 6 or you know all the 8 corners occupied by zinc atoms and the central atom is made up of copper in a third one it may be a different arrangement all together. That means, where as in case of the ordered condition take any unit cell the same type one particular type of lattice positions will be occupied by one particular type of atoms and another particular type of lattice position will be occupied by another kind of atom the situation is totally different when we take this material above 465 C when we say that the material is in the disordered condition.

So, if we look at say just one unit cell above 465 C it may. So, happen that out of the 8 corner positions may be seven are occupied by copper and one of the corner atoms occupied by zinc and that may be a copper in the body centred position in a second unit cell it may. So, happen that five of the corner locations are occupied by copper atoms free of the corner locations as well as the body centred location may be occupied by a zinc atom.

So, in this way, but the all the atoms are arranged in the extended crystal in such a manner that the average composition shows Cu Zn it does not depart from that. So, the composition of the material does not change, but above 465 degree centigrade the arrangement of the atoms at different locations of the unit cell is completely half (Refer Time: 09:46) we say that the material is in what is known as the disordered condition the material is in the disordered condition.

Now, when ordering takes place from disordered Cu Zn or when disordering takes place from ordered Cu Zn what happens to the properties of the material there are subtle changes in properties which we observe during a order disorder transformation for example, Cu Zn when it is ordered condition it has a high value of electrical conductivity in the disordered condition the electrical conductivity is much much lower than the hardness of ordered Cu Zn is higher than the hardness of disordered Cu Zn.

So, we say that due to an order disorder transformation in a material properties do change, but when you look at the microstructure of Cu Zn at a temperature below 465 and also at a temperature above 465 microstructure wise there is no change and of course, composition wise also there is no change, but this kind of transformation leads to

some changes in the material properties.

So, how to figure out whether such a transformation has already taken place or not; that means, it is very necessary to know whether there has been a order disorder transformation in the material because since the composition does not change a microstructure does not change. So, usual ways of finding out the transformation are of no use, but X-ray diffraction provides a unique method by which we can determine the order disorder transformation in materials. Now if we look at Cu Zn in an ordered condition and in a disordered condition you see disordering maybe to a very high extent disordering maybe of a very low extent.

So, how to you know depending on how in the disordered material the atoms are arranged in the unit cells. So, how to determine the degree of order or disorder now as the temperature is raised and the critical temperature t c is approached. So, this temperature is a critical temperature for Cu Zn this temperature is a critical temperature for Au Cu 3 gradually some randomness in atomic arrangement sets in and as we go above the critical temperature more and more this randomness goes on increasing.

So, the departure from perfect order can be expressed by what is known as the long range order parameter which is s equal to X A minus Y A divided by 1 minus 1 by a. So, what is X A is a fraction of a sides which are actually occupied by the right kind of atoms here a atoms and Y A the fraction of a atoms present in the alloy say for example, if we look at the Cu Zn case what it says that s of the degree of order is equal to X A minus Y A divided by 1 minus y a.

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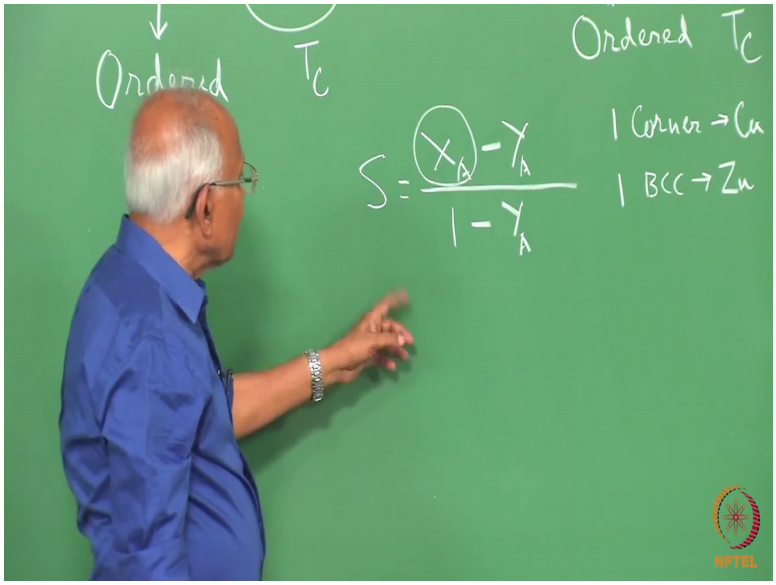

So, what is X A is a fraction of a sides which are actually occupied by the right kind of atoms now what are the 2 different sides available to the copper and zinc atoms in a unit cell of Cu Zn one corner side one corner site in the ordered condition by copper atoms and one body centred cubic side to be occupied by zinc atoms.

So, it says that long range order parameter can be determined by expression where X A is the fraction of a sides which are actually occupied by the right kind of atoms here a atoms. So, what is the fraction of corner sides occupied by copper in a perfectly ordered alloy one in a perfectly ordered alloy the X A the type of a particular side the fraction of the right kind of atoms to occupy that particular side is one fraction, because in order case all the corner atoms are occupied by copper. So, the value of X A simply becomes 1.

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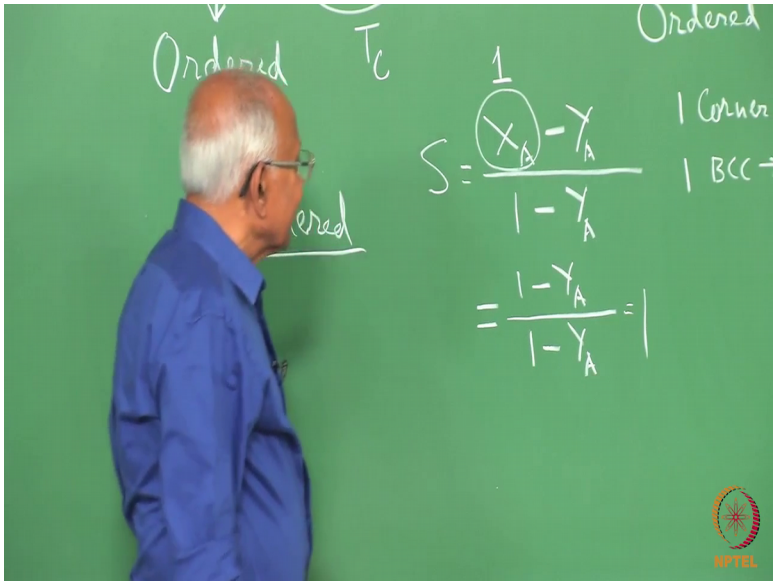

So, in case of ordered Au Cu 3 in case of ordered I am sorry ordered Cu Zn the degree of order is equal to X A minus Y A by 1 minus Y A where X is a fraction of a particular side which is actually occupied by the right kind of atom. So, here the fractions of corner sides are occupied by copper. So, entire this fraction all the corner sides occupied by copper in ordered condition, so, this fraction is equal to 1.

And what about Y A; Y A is the fraction of a atoms present in the alloy anyway. So, because this is one; so, s for an ordered Cu Zn or an ordered Au Cu 3 will be 1 minus Y A divided by 1 minus Y A equal to 1. So, we say that the degree of long range order s that for a completely ordered material we will have the s parameter equal to 1. Now when we are talking about the compound Cu Zn what will happen to the X-ray diffraction pattern of Cu Zn when it is in a completely ordered condition and in completely disordered condition we are going to find out say for example, when Cu Zn is perfectly ordered.

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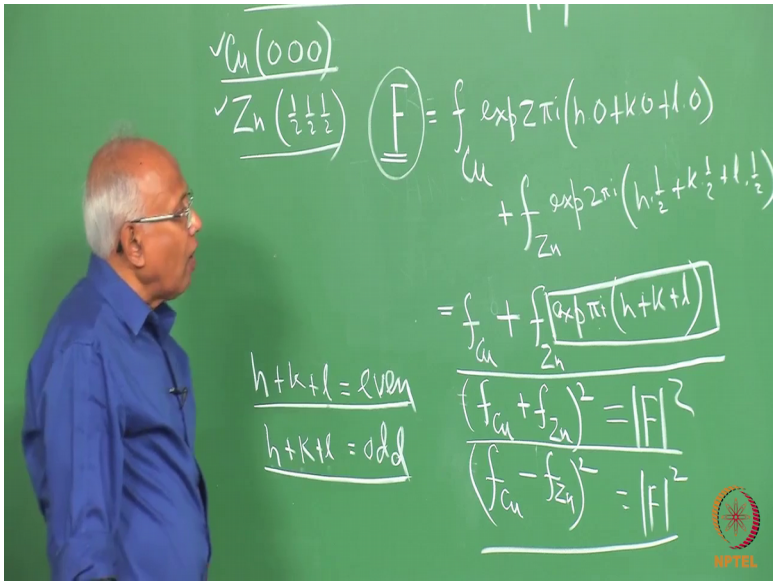

So, when Cu Zn is perfectly ordered then we know that one corner side with fractional coordinates 0 0 0 will be occupied by copper. So, copper will be 1 1 copper atom at the fraction of side 0 0 0 and there will be a zinc atom at the fraction of side half half half.

So, when Cu Zn is in a perfectly ordered condition then what will happen to the crystal structure factor of the material? So, crystal structure factor of the material will be the equal to f times and you see here there are 2 kinds of atoms. So, the atomic scattering factors of these 2 atoms will be different. So, when we look at the crystal structure factor and find it out for all the atoms belonging to the unit cell then. So, for as the copper atom is concerned it is f c u exponential 2 pi i into h equal to 0 plus k equal to 0 plus l equal to 0 plus now we talk about the zinc atom. So, it is f z n for the zinc exponential 2 pi i h into half plus k into half plus l into half.

So, it will be f c u exponential this will be 0. So, this value will be simply one exponential 2 pi i into 0 it will one. So, f c u plus f z n exponential pi i into h plus k plus l now this is the crystal structure factor for a unit cell of order Cu Zn. Now there can be 2 situations arising in one case h plus k plus l can be an even quantity. So, if h plus k plus l is an even quantity then what will happen to this expression exponential pi into h plus k plus l it will be plus 1. So, it will be f c u plus 1 into f z n. So, it is f z n what is the other

possibility h plus k plus l is equal to an odd quantity h plus k plus l is equal to odd quantity. So, what will happen when h plus k plus l is an odd quantity this expression will be simply equal to minus 1 as a result the value of f will be equal to f c u minus f z m. So, you see that when Cu Zn is in a perfectly ordered condition in the sense that all corner atoms are occupied by c u copper atoms and all body centred positions are occupied by zinc atom.

Then we figure out that f the crystal structure factor for unit cell of order Cu Zn will be equal to f c u atom scattering factor of copper last plus f z n the atomic scattering of zinc when h plus k plus l is an even quantity and it will be f c u minus f z n when h plus k plus l is an odd quantity now you see that in the intensity equation f will always appear in the form of f square f will always appear in the form of f square.

So, whether h plus k plus l is even or odd the square of these terms will always be positive which means diffracted intensity will be produced from plains for which h plus k plus l are even and also from the planes for which h plus k plus l is equal to odd. So, this is a very important observation. So, simply by calculating the value of crystal structure factor for ordered Cu Zn we find that the value of the crystal structure factor will be f c u plus f z n when h plus k plus l is an even quantity and it will be f c u minus f z n when h plus k plus l is an odd quantity.

So, from all kinds of planes there will be diffraction because in the diffracted intensity f appears as f square as we know. So, you know the square of this quantity and the square of this quantity are all positive are all positive now the value of this quantity f square in this case is much higher than over there the value of this, this value is much larger than this value. That means, some of the lines their intensity will be much higher and which are those planes those are the h k h plus k plus l is even planes, but those planes for which h plus k plus l is odd for then the intensity will be proportional to this square which will be less than in the previous case.

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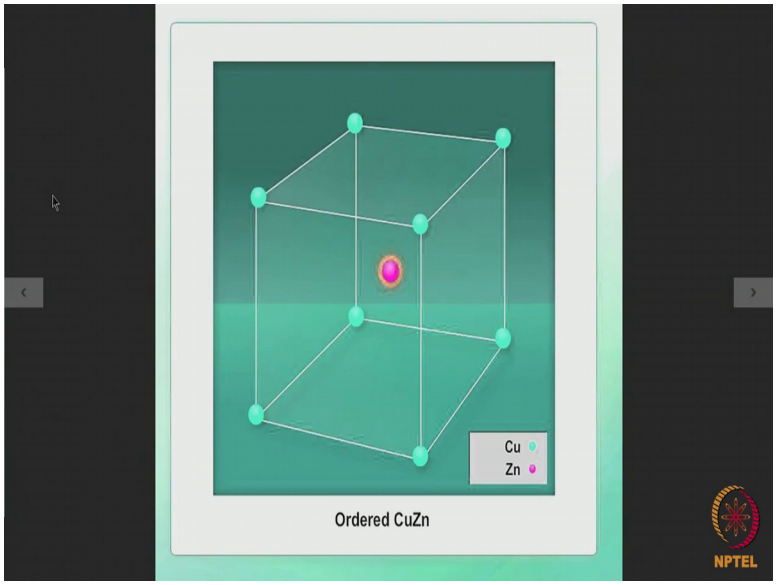

Now, we will examine the situation where Cu Zn is in the disordered condition. So, now, we will examine the situation where Cu Zn is in the disordered condition here depending on the large number of unit cells the arrangement of the copper and zinc atoms, so, far as the respective sides are concerned can be very very different, so under such circumstances how. So, we study this material. So, what we want to do now just as for copper zinc ordered condition we try to figure out the value of crystal structure factor and from there we try to determine from which h k l planes the diffracted intensity will be much higher than from other planes in a similar manner we will try to find out the value of crystal structure factor f for Cu Zn in the disordered condition.

Now, let us see how we can do that you see when the material is in a completely disordered condition the situation changes from one unit cell to another. So, how do we know the exactly which atoms are occupying which types of sides in this particular case in order to avoid the difficulty we assume that when Cu Zn is in a disordered condition.

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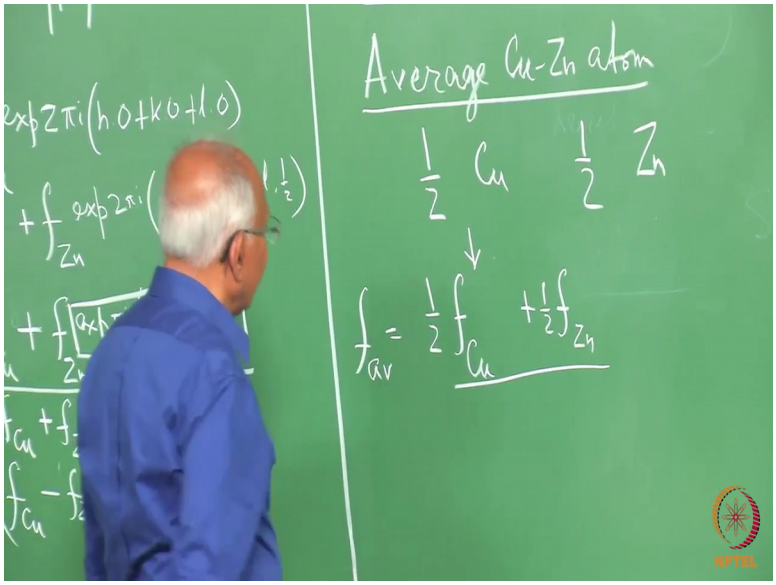

When Cu Zn is in a disordered condition we can consider each lattice point to be occupied by what is known as an average copper zinc atom an average copper zinc atom you see from unit cell to unit cell the situation will be different in some unit cell you know seven corner atoms may be occupied by copper atoms then one of the corner atoms will occupied by zinc body centred atomic occupied by copper in some other it is again a different kind of element in some other again a different kind of arrangement the only thing that we know that the composition of the material as a whole does not change.

So, we can consider as if in Cu Zn disordered condition we have what is known as an average Cu Zn atoms and what kind of characteristics this average Cu Zn atom will be from chemical composition we find per unit cell there is a one copper and one zinc atom. So, we can say that an average copper zinc atom will have half the characteristic of copper and half the characteristic of zinc. So, an average copper zinc atom we can take as one which will have half the characteristic of copper and half the characteristic of zinc. So, what will be the atomic scattering factors for this it will be half f c u plus half f z n. So, we say that this will be the atomic scattering factor for an atom which is a average copper zinc atom.

So, f average for this average Cu Zn atom will be equal to half f c u plus half f z n.

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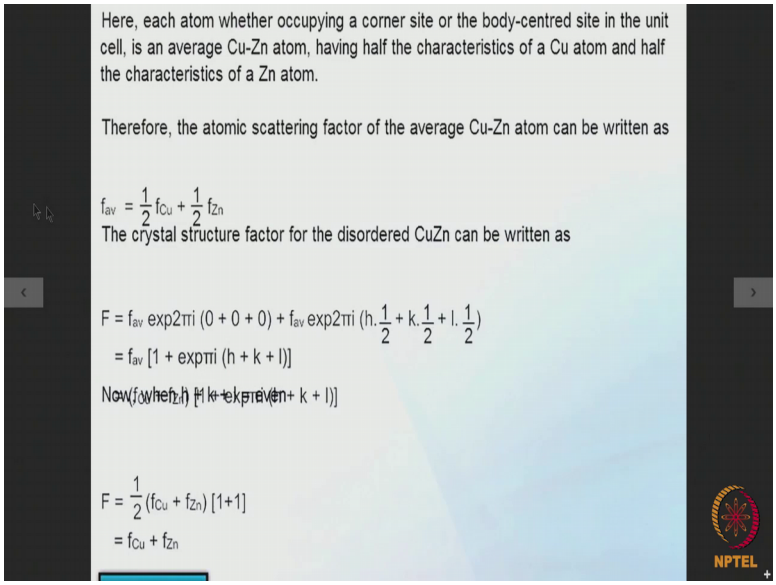

Now we can calculate the crystal structure factor f for disordered Cu Zn now if we do that we can write capital f is equal to now there are 2 atoms one is at 0 0 0 location the other one at half half half location and we have got average Cu Zn atom at both locations. So, we can write capital f is equal to f average into exponential 2 pi i h into 0 plus k into 0 plus l into 0 plus f average exponential 2 pi i into h into half plus k into half and l into half. So, this is equal to f average into 1 plus exponential pi i h plus k plus l. So, you see that the crystal structure factor in the disordered condition for Cu Zn.

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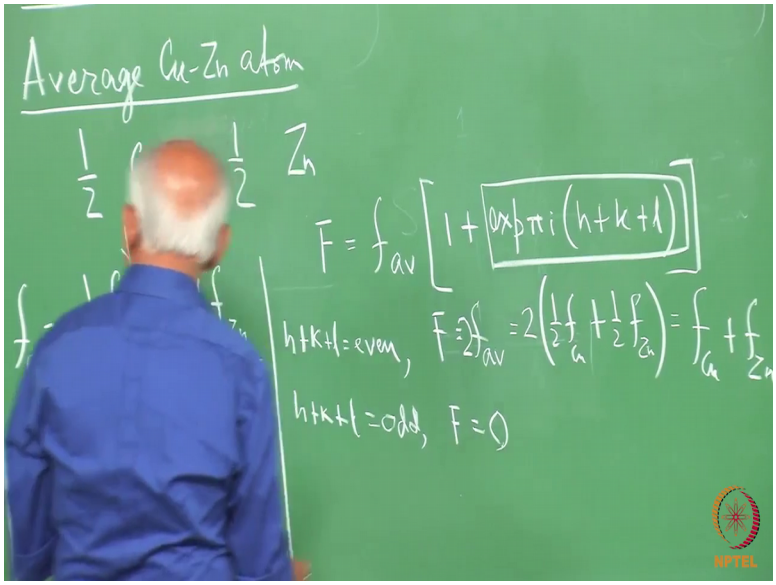

It can be written as f average into 1 plus exponential pi i in to h plus k plus l by again if you look at the situation where h plus k plus l is equal to an even quantity where h plus k plus l is an even quantity then what will happen to this expression.

If h plus k plus l is even quantity then this term here will have the value of plus 1. So, capital f will be equal to f average into 1 plus 1 two. So, it will be 2 times f average, but we know that what is f average f average is half f c u plus half f z n. So, we can write 2 into half f c u plus half f z n. So, that will give us the value of f c u plus f z n what about when h plus k plus l is equal to an odd quantity. Now in this expression this will become minus 1 if h plus k plus l is an odd quantity this will have value of minus 1. So, capital f will have a value of f average into 1 minus 1; that means, capital f becomes equal to 0.

So, we see a very clear cut case that when you have when you have planes atomic planes for which h plus k plus l is an even quantity then for the ordered Cu Zn f becomes equal to f c u plus f z n. So, that f square becomes f c u plus f z n square when we come to the disordered Cu Zn again we find that f becomes equal to f c u plus f z n.

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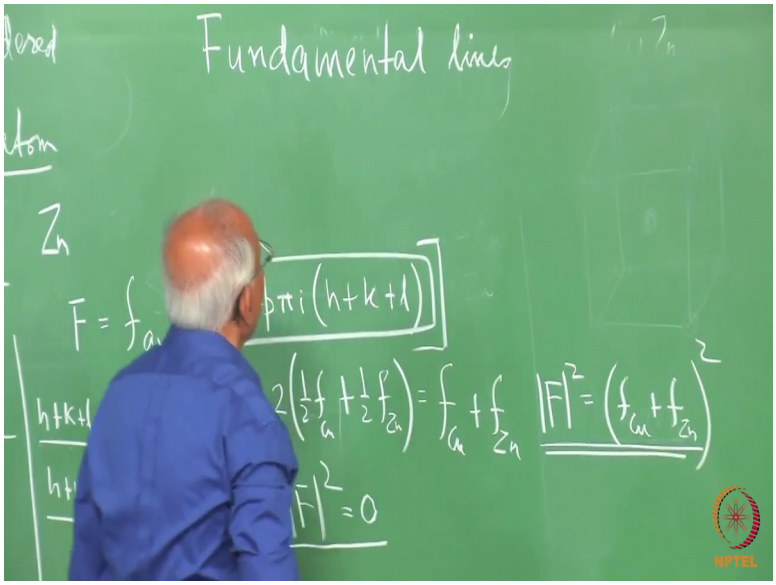

And therefore, in this case also capital f square will be equal to f c u plus f z n square. So, this is the same value as we get over here. So, it says whether Cu Zn exits in the ordered form or in the disordered form we will say that the crystal structure factor for atomic planes for which h plus k plus l is equal to an even quantity will be the same for example, f c u plus f z n.

What happens when we look into those planes for which h plus k plus l is an odd quantity now when the material is in the ordered condition for h plus k plus l is equal to odd we find that f square is f c u minus f z n square what happens in the disordered condition well f is equal to 0. And therefore, f square is equal to 0. So, you say that f square appears in the equation for integrated intensity. So, naturally if f square is 0 there will be no intensity. So, what does this you know calculation shows we find that if you have Cu Zn in an ordered condition and in the disordered condition there will be a strong diffracted intensity from those planes for which h plus k plus l is an even quantity both in the respect ordered as well as disordered Cu Zn.

On the other hand if we consider for the planes for which h plus k plus l is a odd quantity we will find that the diffracted intensity from those planes will also be there in case of the ordered material, but the diffracted intensity will simply be 0 in case of the

disordered material. That means, the ordered material will show diffraction lines from planes for which h plus k plus l is even as well as from planes for which h plus k plus l is odd on the other hand when Cu Zn is in the disordered condition then the diffraction will occur where h plus for those planes for which h plus k plus l is even and there will be no diffraction taking place from h plus k plus l is equal to odd planes.

So, you say that if we have 2 diffraction patterns one for ordered Cu Zn and the other one for disordered Cu Zn then the ordered material the diffraction pattern of the ordered material will show lot more lines why because both type of planes for which h plus k plus l is even and h plus k plus l is equal to odd will give raise to diffraction on the other hand the disordered structure if you taka diffraction pattern will show fewer lines because here only diffraction will occur for those planes for which h plus k plus l is an even quantity no diffraction will take place from planes for which h plus k plus l is an odd quantity.

So, the diffraction pattern of an ordered material shows lot more lines as compared to the diffraction pattern from a disordered material. Now you see the value of f square here you know may be very very low then over here. So, we say that for those planes for which h plus k plus l is equal to even the intensity values of the lines appearing in the diffraction pattern of both the materials will be of similar degree, but when it comes to the h plus k plus l odd links in the ordered material they will give a week intensity for such planes and over here the intensity will not be there; that means, those lines will be absent.

In a similar way we can do the calculations for what is the difference between the diffraction pattern from ordered Au Cu 3 and disordered Au Cu 3. So, you say that the lines which are common in the ordered and disordered Cu Zn the common lines are known as the fundamental the fundamental lines, lines are common in the X r d of both ordered and disordered Cu Zn the extra lines which appear in diffraction pattern of the ordered material.

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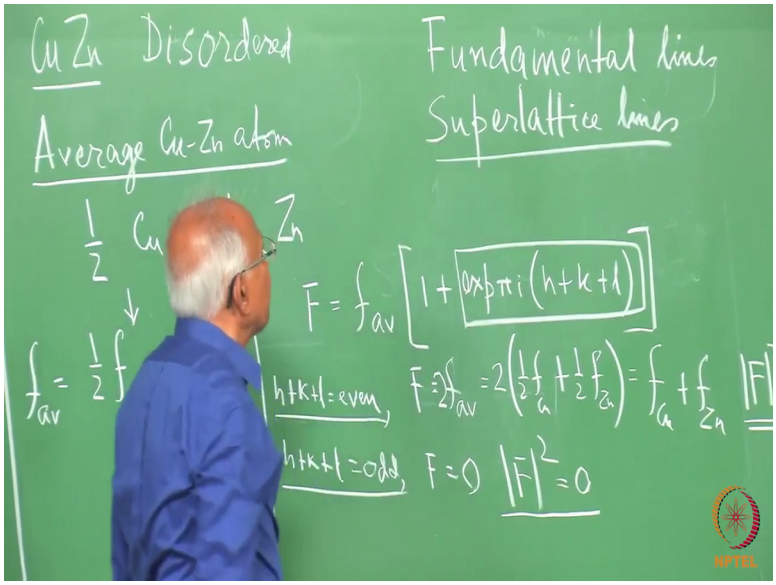

Those are known as the super lattice lines those are known as the super lattice lines; obviously, the intensity of the super lattice lines will be much less as compared to the fundamental lines because of this reason you know here f c u it is f c u plus f z n square in case of h plus k plus l is even and in this case when h plus k plus l is odd f square f c u minus f z n square naturally the super lattice lines are much weaker compared to the fundamental lines.

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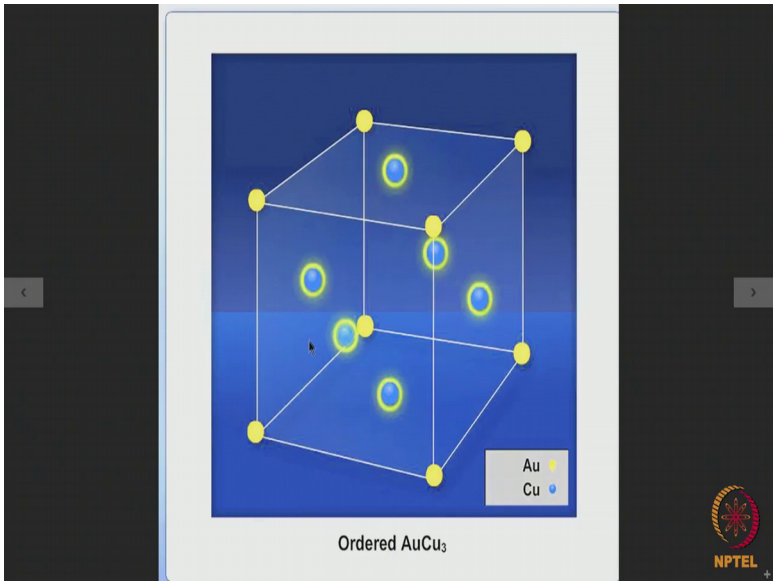

Now, we can do a similar exercise for the ordered Au Cu 3 and disordered Au Cu 3 you see in an ordered Au Cu 3 material the corner sides will be occupied by the gold atoms and the face centred positions are occupied by the copper atoms. So, the chemical you see one corner atom plus 3 of gold and 3 face centred atoms of copper. So, there are four atoms per unit cell in this particular case.

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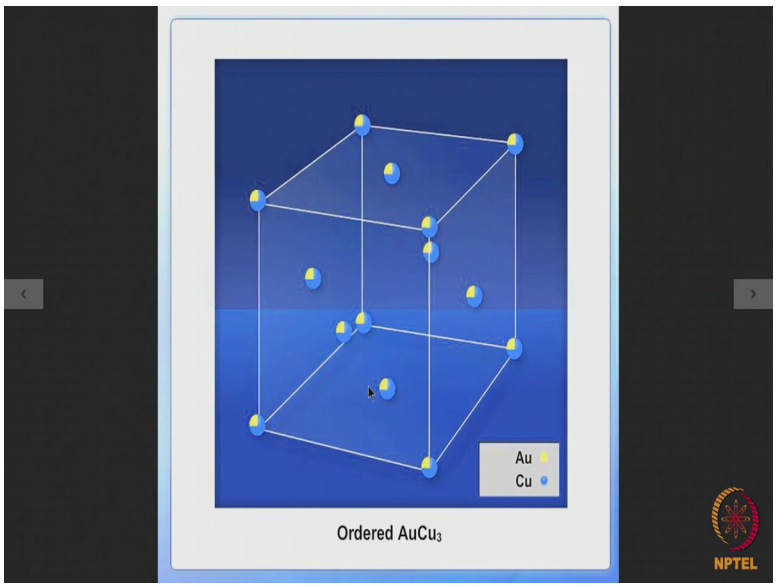

Now in the disordered case what will happen again we have a difficult situation because arrangement will vary from you know unit cell to unit cell; so we consider an average gold copper atom and because the chemical composition is Au Cu 3.

So, there are there is one gold atom out of four atoms present in the unit cell and 3 copper atoms out of four in the unit cell we say that now we have an average atom at all the lattice locations and this will have one fourth the characteristic of gold and 3 fourth the characteristic of copper. You can say that the copper atoms are blue colours and gold atoms are yellow colours. So, each average atom we will consider to be made up of such that one fourth is a characteristic of gold one and 3 fourth is the characteristic of copper.

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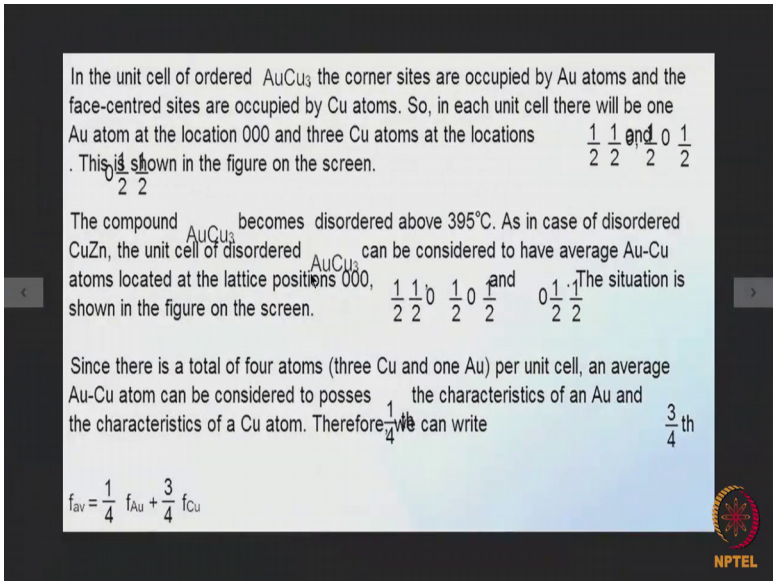

And again as we did with respect to Cu Zn we know that the in case of ordered Au Cu 3 in case of ordered Au Cu 3 we can find out that the corner locations are 0 0 0.

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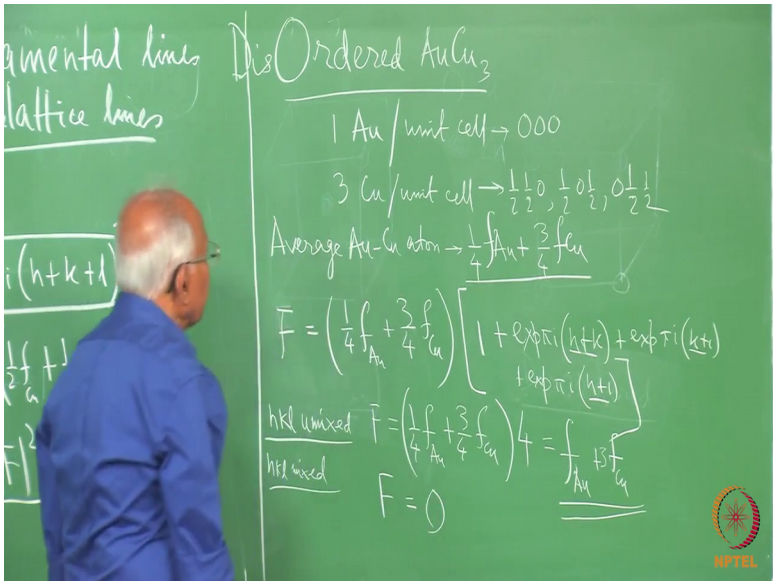

So, for ordered Au Cu 3 ordered Au Cu 3 we know that the corner sides are occupied by the gold atoms and. So, there will be one gold atom per unit cell and there will be copper atom per unit cell and what are the fractional coordinates this one gold atom structural coordinates are 0 0 0 and what about this 3 copper atoms per unit cell half half 0 half 0 half and 0 half half. So, in case of the ordered Au Cu 3, since an average Au Cu atom has got one fourth the characteristic of gold and three fourth the characteristic of copper then the average gold copper atom will have an atomic scattering factor given by one fourth f a u plus 3 fourth f c u. So, this will be the atomic scattering factor for the average gold copper atom.

So, if we now write down an expression for capital f crystal structural factor. So, it will be one fourth f a u plus 3 fourth f c u then yeah well yeah this is the thing. So, let us talk about the disordered Au Cu 3 first what I am doing is for the disordered Au Cu 3 first. So, for the disordered Au Cu 3 we will have an average gold copper atom at all the locations 0 0 0 half half 0 half 0 half and 0 half half. So, we will have a situation where the f can be written for disordered Au Cu 3 this manner it will one fourth f c u f a u plus 3 fourth f c u multiplied by you know exponential 2 pi i into h into 0 k into 0 plus l into 0. So, it will be simply equal to 1 plus we can write down for the other 3 locations exponential pi i into h plus k plus exponential pi i k plus l plus exponential pi i h plus l.

So, you see that this is the expression for the capital f for the disordered Au Cu 3.

Now, if h k l are unmixed if h k l are unmixed; that means, all are odd or all are even then what will happen if h k l are unmixed; that means, all are odd or all are even in that case h plus k k plus l h plus l these are all even quantities. So, their values are 1 plus 1 plus 1 and plus 1. So, when h k l are mixed quantities capital f will be equal to f one fourth f a u plus 3 fourth f c u multiplied by four. So, it will be equal to f c u plus 3 f c u. So, this will be the value of crystal structural factor in case of the disordered Au Cu 3 when h k l are unmixed, but when h k l are mixed what will happen when h k l are mixed; that means, some are odd some are even then what will happen out of these 3 quantities one will be plus 1 the other 2 will be minus 1 as a result the value of capital f will be simply equal to this quantity multiplied by 0 that is 0.

So, you say that when we have Au Cu 3 in a totally disordered condition then when we have a completely disordered condition therefore example, it was written ordered Au Cu 3 it is not true it is a disordered Au Cu 3 and that is why we have taken an average gold copper atom at all the lattice sides. So, if we do that what we find in the disordered condition when h k l are unmixed quantities the value of capital f is f a u plus 3 f c u on the other hand for all cases h k l are mixed quantities we find f becomes equal to 0. So, it shows that when Au Cu 3 exists in the disordered form then we will have diffraction lines only from those planes for which h k l are unmixed quantity and no diffraction line from all those planes where h k l are mixed quantities.

Now, if we find out the values of f for ordered Au Cu 3 then what will happen in case of ordered Au Cu 3 we know that the corner atoms are occupied by the gold atoms corner locations are occupied by the gold atoms and face centred positions are occupied by copper atom.

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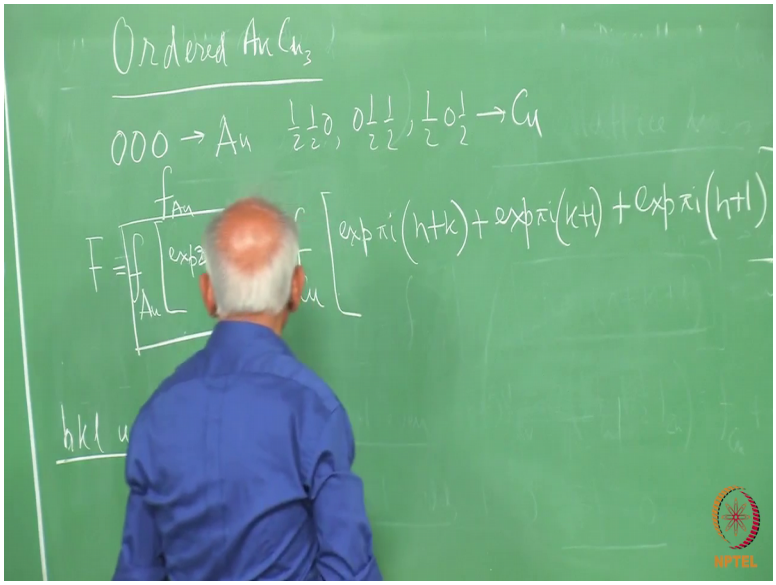

So, if now we talk about ordered Au Cu 3 we know that the 0 0 0 locations the corner locations will be occupied by the gold atoms where as half half 0 0 half half and half 0 half locations will be occupied by copper atoms. So, in this case if we want to figure out what the value of capital f is going to be then we have to do the summation over one gold atom. So, f a u into exponential 2 pi i into h into 0 plus k into 0 plus l into 0. So, the whole thing will be 0 here plus f c u we will have exponential 2 pi i h into half plus k into half plus l into 0 etcetera, etcetera. So, it can be written as exponential pi i in to h plus k plus exponential pi i into k plus l plus exponential pi i into h plus l.

Now, again we find that and this value is simply equal to 1 because exponential 2 pi i 0 is simply equal to 1. So, we can write down you know instead of this we can write down simply f a u. So, now, let us consider 2 different cases in one case say h k l are unmixed quantities when h k l are unmixed quantities then what will happen either all odd or all even then this will be an even quantity this will be an even quantity this will be an even quantity. So, the value of this will be 1 plus 1; this will be the value of plus 1 plus 1.

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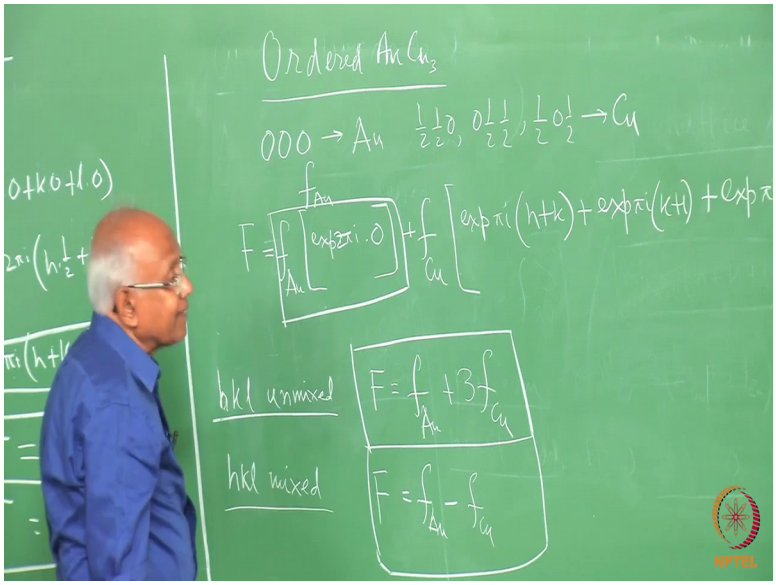

So, you say that when h k l are unmixed capital f becomes simply equal to f a u plus 3 f c u. So, this is the value of the crystal structural factor when h k l are unmixed in case of an ordered Au Cu 3.

What happens when h k l are mixed quantities what happens when h k l are mixed quantities when they are mixed quantities one of these will be you know plus 1 1 of these will be even other 2 will be odd as a result it will be 1 minus 1 minus 1. So, we will find that it will be simply capital f is equal to f a u minus f c u.

So, you see that when we consider the disordered Au Cu 3 we find that diffraction will be possible from only those planes for which h k l are unmixed no diffraction will happen from those planes for which h k l are mixed because f is 0. On the other hand when the material is in the ordered condition then diffraction will take place not only from the planes for which h k l are unmixed, but also from the planes for which h k l are mixed and as usual the lines which will be obtained from planes having h k l unmixed quantities in both the patterns are known as the fundamental lines when we consider the h k l unmixed planes we will have diffraction taking place from those planes both in the ordered condition and in the disordered condition.

However, when we talk about the h k l mixed planes there will be diffraction from those

planes in case of the ordered alloy, but not in case of the disordered alloy. So, as a result we will see the number of line diffraction which will appear in the diffraction pattern of ordered Au Cu 3 will be more than the number of lines which appear in the diffraction pattern of disordered Au Cu 3. And this is the way we can distinguish an ordered material and the disordered material the ordered materials will show more number of lines the fundamental lines as well as the super lattice lines, but in the disordered material only the fundamental lines will be obtained not this lattice points.

So, absence of super lattice lines in the diffraction pattern of disordered Cu Zn or Au Cu 3 will show that those are in a disorder state. So, absence of the super lattice lines from the diffraction pattern of Au Cu 3 or Cu Zn will indicate that those are in a disordered condition.