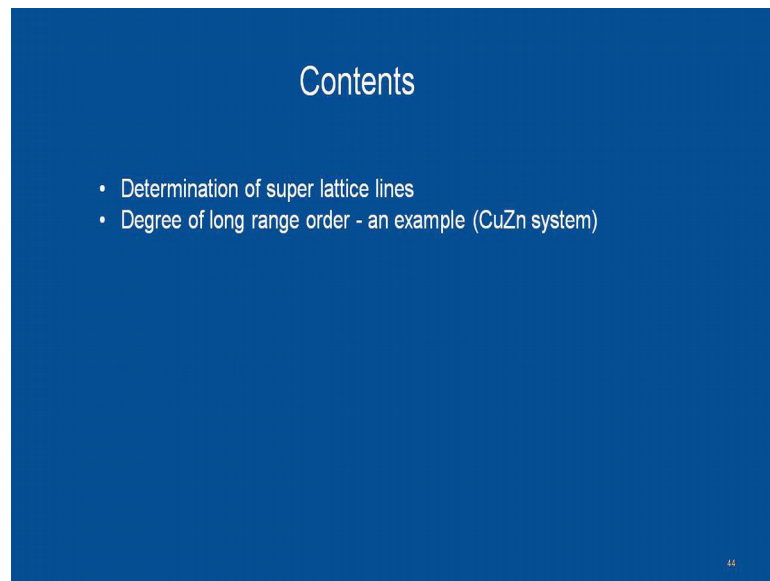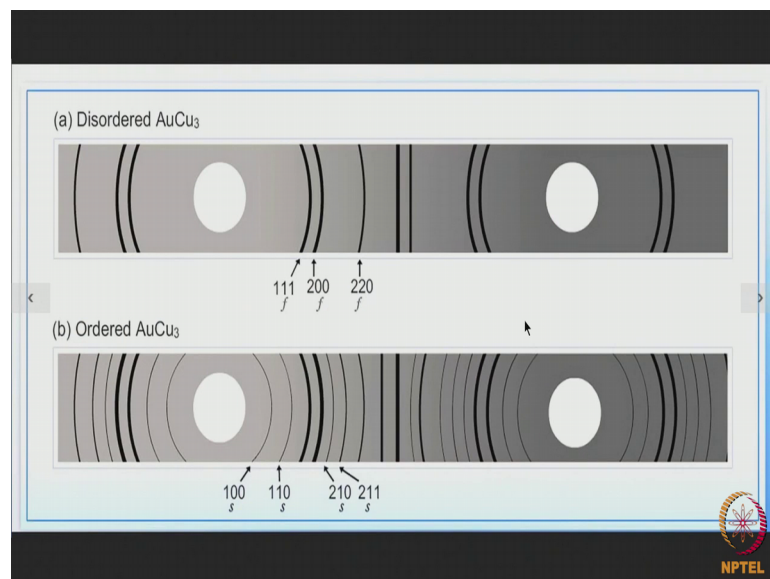# X-Ray Crystallography
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Lecture - 21
Ordered Disordered Transformation - continuation

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The diagram here shows the x-ray diffraction patterns taken from a disordered AuCu 3 and ordered AuCu 3. Now, if you examine these two patterns, we will find some of the lines are common to both say for example, the line here 1 1 1, this 2 0 0 and this 1 2 2 0, they appear in the diffraction pattern for the ordered AuCu 3 also. So, these common lines which appear in the x-ray diffraction pattern for ordered AuCu 3 as well as disordered AuCu 3 are known as the fundamental lines as I have already explained.

Now, in addition to these in the ordered material, the XRD pattern shows many extra lines. For example, here is 1 0 0. S stands for superlattice and here F stands for fundamental. So, you say that here it is 1 0 0, then 1 0 0 2 1 0 2 1 1 etcetera and there are many others which appear in the diffraction pattern of ordered AuCu 3 only, but not in that of disordered AuCu 3.

So, the extra diffraction lines which appear in the XRD pattern of an ordered material, these extra lines are known as the superlattice lines. Now, looking at this diagram, it immediately becomes quite apparent that the intensities of the superlattice lines are much less than that of the fundamental lines. We can even do an order of magnitude calculation regarding the intensities of the fundamental and superlattice lines.

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For example, we have already seen that in case of a fundamental line in the XRD pattern of an ordered material.

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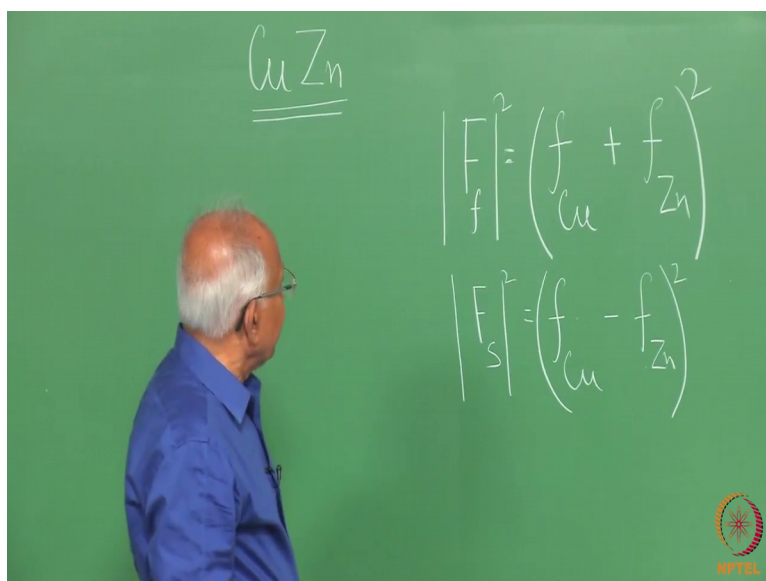
We have F is equal to say let us take a particular example here say for example, if you take particular case say CuZn. Let us consider a particular case CuZn which can exist in both ordered and disordered condition.

So, if we look at the crystal structure factor F for the fundamental lines, it is equal to f C u plus f Z n. So, it is equal to f C u plus f Z n. So, naturally if we make square on both sides intensity of the fundamental lines in order, CuZn will be square of this. On the other hand, if we look at superlattice line, then F s is equal to we have already seen f C u minus f Z n. So, if we make the square it will be f C u minus f Z n square. Now, the F square values appear in the intensity equation for the diffraction lines as we have already seen. Therefore, if we want to find out the intensity of a superlattice to a fundamental line, this is how we can proceed say for example.
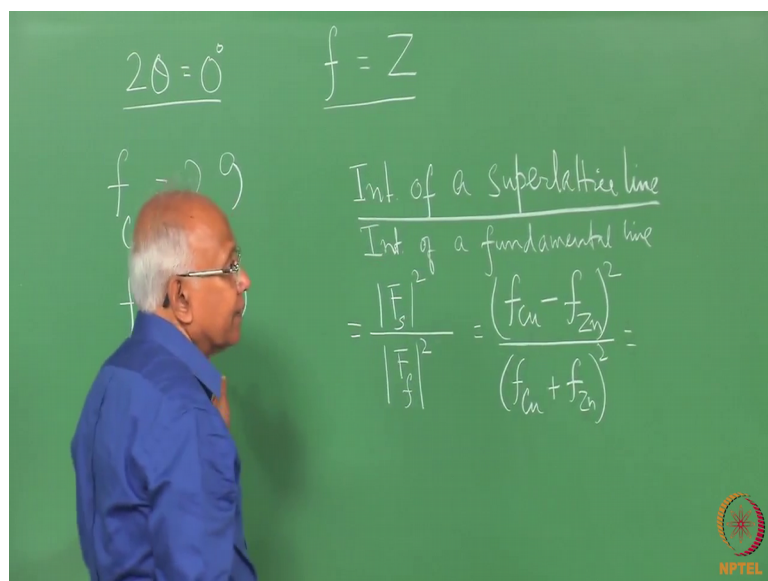
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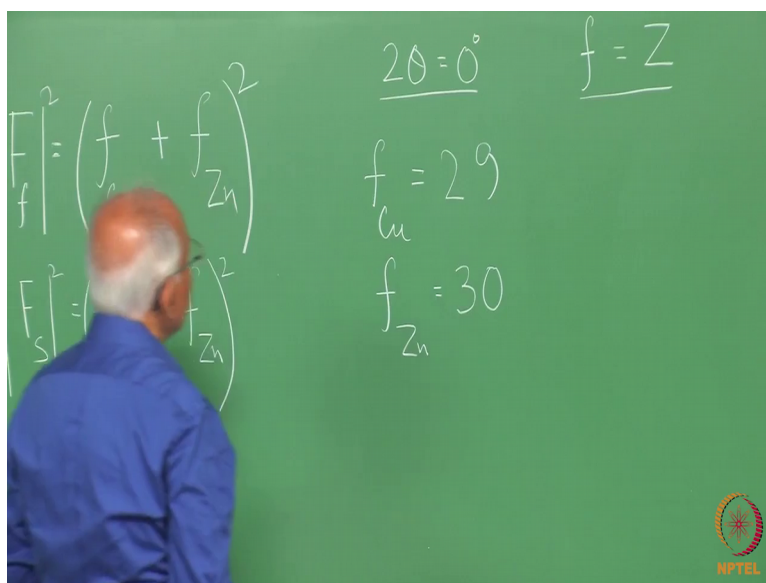
Let us assume that diffraction takes place from ordered CuZn in a direction very close to the forward direction and that is 2 theta is equal to 0 very close to that in the forward direction.

Now, we know that for scattering taking place in the forward direction, atomic scattering factor of an element becomes equal to its atomic number. When scattering takes place in the forward direction, atomic scattering factor of the scattering atom f becomes equal to its atomic number z. So, if we are looking at the diffraction taking place from CuZn in an ordered condition in a direction very close to the forward direction, we can assume that f copper will be very similar, almost the same as it is atomic number and the atomic number is 29. So, it will be f you know the atomic scattering factor is 29 for copper atoms. Similarly, f Z n will be equal to the atomic number for zinc. So, we can write it as 30.

Now, we can calculate intensity of a superlattice line divided by intensity of a fundamental line equal to F s square divided by F f square and that is equal to f C u minus f Z n square divided by f C u plus f Z n square.
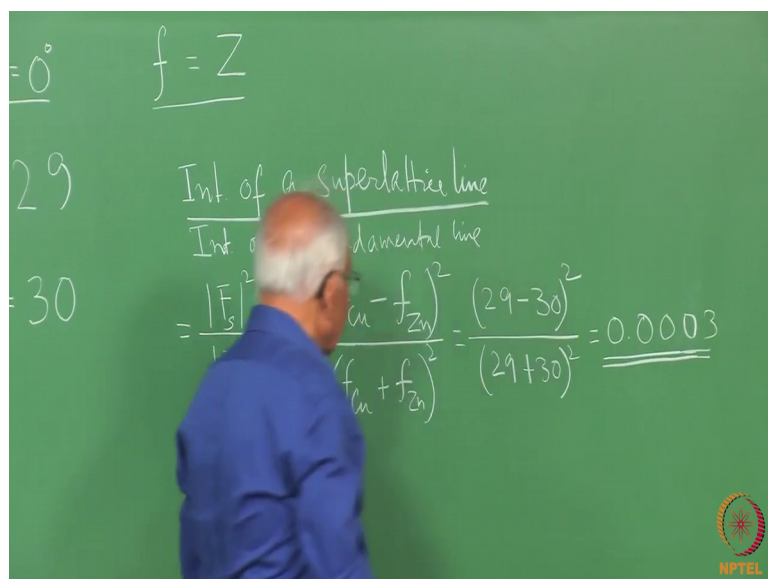
So, if we put the values for that particular diffraction in a direction very close to the forward direction, we can write this will be equal to 29 minus 30 square divided by 29 plus 30 square and that becomes equal to something like 0.03. So, it becomes something like I am sorry. It will be triple 0003. So, this ratio is 0.003. So, we say that in this

particular case, we have assumed that all the different factors which influence the intensity of a diffraction line except in f are the same and that is the reason why we have taken only the crystal structural fact into consideration and on that basis, we find that the superlattice lines where intensities are much less compared to the fundamental lines in case of the particular material which is CuZn.

You see whenever the material we are examining is made up of atoms which are very close in their atomic number; this kind of situation will arise. That means, the intensity of the superlattice lines will be much less compared to those of the fundamental lines and this may create a problem if we use the Debye Sherrer method. The weak superlattice lines we may not be able to recognise them from the back ground if they almost match with the background and those will not be visible, but if the material is made up of two elements having every different x values, then this problem will not arise.

In such cases, where ordering takes in a material made of elements of very close atomic number, and then x-ray diffraction may not be the right kind of method for finding out the order disorder transformation.
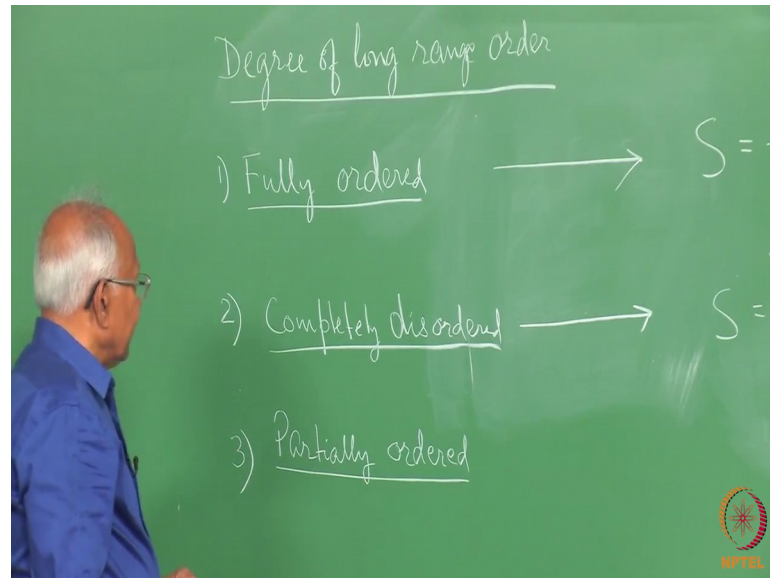
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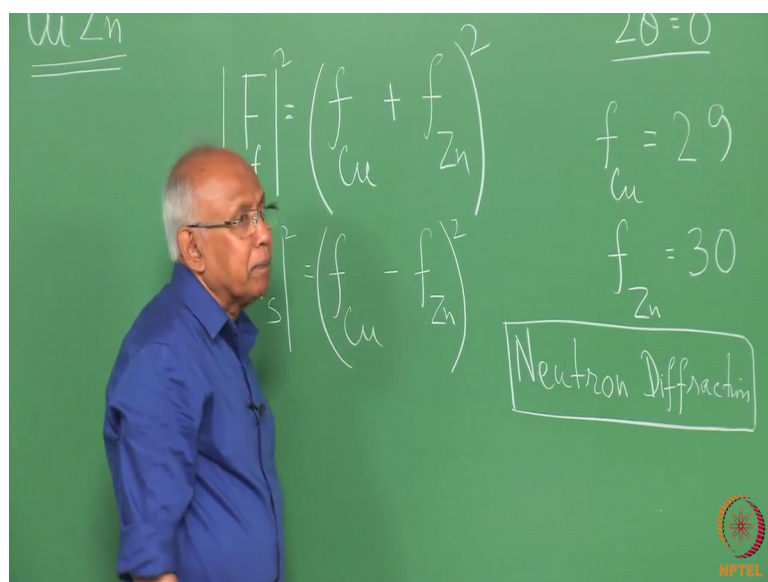
In such cases, neutron diffraction maybe a better option because scattering factors of two elements very close to each other in the periodic table may have very different scattering factors for neutrons. So, in those cases maybe neutron diffraction will be a better method to use.
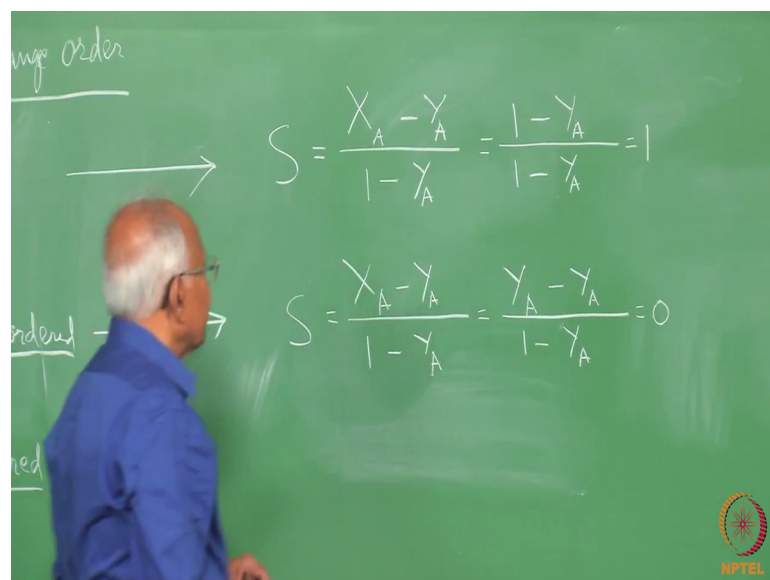
I shall now concentrate on measuring the degree of order degree of long range order in a material which is fully ordered in a material which is completely disordered and in a material which is partially ordered.

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Now, we will examine these three cases one after another.

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We know that the long rage order parameter S can be written as the ratio X A minus Y A divided by 1 minus Y A, where X A is the fraction of A sides which are actually occupied by A atoms and Y A is the fraction of A atoms in the alloy. Then, for the three different

situations, we can now find out what should be the value of S. Now, when it is fully ordered, we know that the fraction of A sides which are actually occupied by A atoms is equal to 1 because all A sides will be occupied by A atoms. So, in this case as you have seen earlier also, we can write it 1 minus Y A divided by 1 minus Y A equal to 1. So, the value of the long range order parameter S is equal to 1 in case of a fully ordered material.

Now, if the material is completely disordered, then what happens again, this is the expression and here number of A sides occupied by A atoms. The maximum fraction of you know the maximum fraction X A can be equal to the fraction of A atoms actually present in the material. So, here what happens is, this ratio becomes X A becomes the same as Y A. So, we can write it as Y A minus Y A divided by 1 minus Y A. It becomes equal to 0. So, we say that if we have a completely disordered material, then the long range parameter S, its value is 0. Now, let us consider a third situation say for example, we have CuZn.

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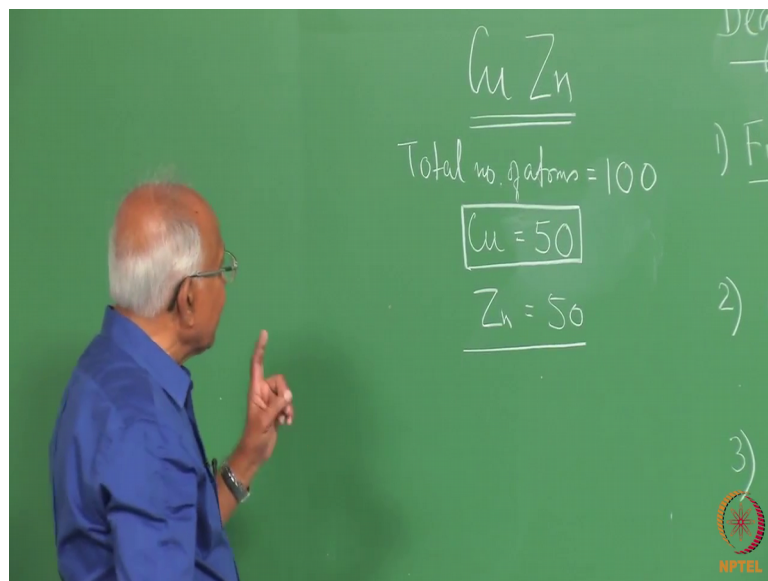
We have CuZn material and naturally if the total number of atoms is equal to 50, for each type of atoms I will rather change the statement say we take CuZn say total number of atoms in this material is 100. Out of these 100 atoms, copper atoms are 50 in number, zinc atoms are 50 in number. Now, we know that 50 copper atoms will lie the 50 copper atoms. They will occupy the corner sides if the material is completely ordered, but let us consider a case that out of 50 copper atoms, only 40 of them are present in their corner
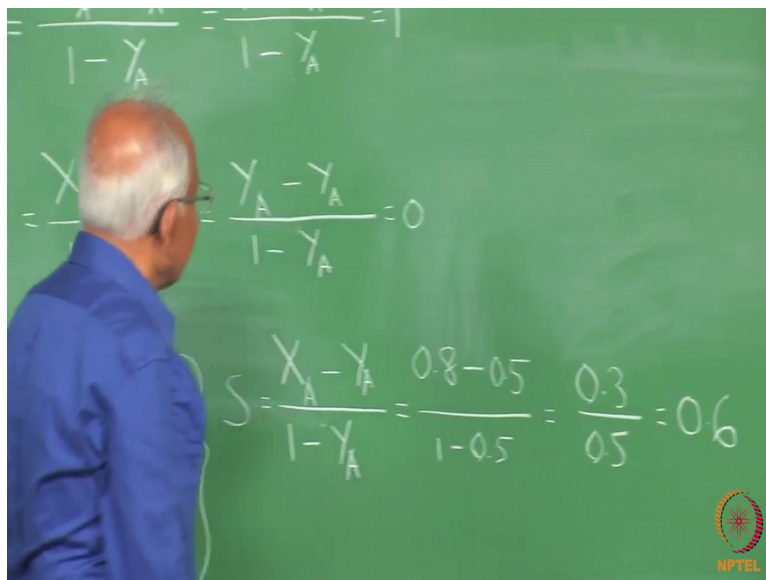
sides. 10 are present in the body centred sides.

So, we do not have a completely ordered CuZn in the sense that out of 50 copper atoms, only 40 actually occupy the corner sides of the unit cells. You know if you completely ordered, all the 50 would have occupied the corner sides, but it is partially ordered. So, say for example, only 40 out of 50 are occupying the corner sides. Now, what should be the degree of ordered in this particular case?

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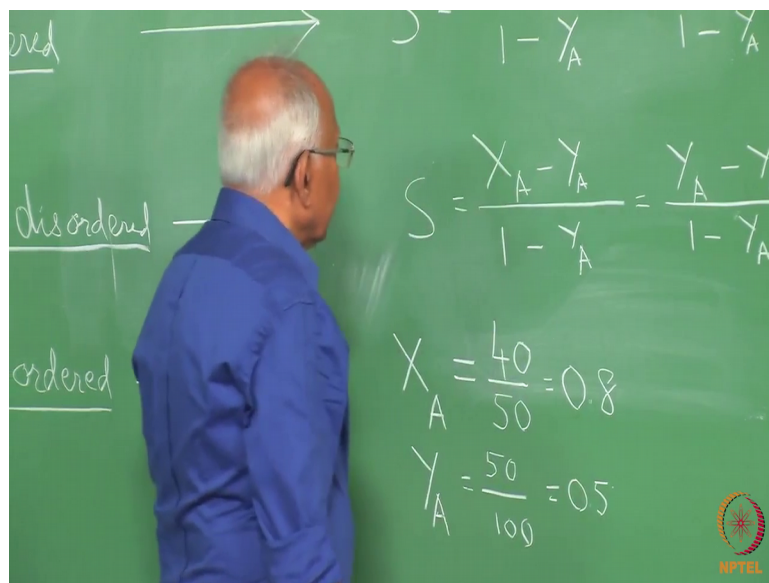
Now, in this particular case, we know that X A the fraction of A atoms actually occupying A sides. So, in this particular case, out of 50, only 40 are actually occupying the corner sides. So, the fraction of copper atoms which occupy the corner sides is equal to 0.8 and the fraction of copper atoms actually present in the material, this is equal to 50 out of 100. So, the material contains 100 atoms and only 50 are copper atoms.

So, Y A becomes equal to 0.5. So, in this case what is the value of S? S is equal to X A minus Y A divided by 1 minus Y A. So, this is equal to 0.8 minus 0.5 divided by 1 minus 0.5. It is equal to 0.3 divided by 0.5. It comes to 0.6. So, we say that in the particular case, we consider here of a copper zinc alloy where the total number of atoms is 100. So, copper atoms are 50, zinc atoms are 50 and if it happens that only 40 out of these copper atoms occupy the corner sides in fully ordered or 50 copper atoms would have occupied corner sides only if we have a situation where the material is not fully ordered.

So, out of 50, only 40 are occupying corner sides. So, in that case how do we determine the long range order parameter value?