Symmetry and Structure in the Solid State
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Lecture – 27
Crystal Structure of Calcium Carbonate

So, we start discussing the space group *P mcn* as we concluded in the previous section. That we have now an enough knowledge of the way in which the diagram which is consisting of symmetry elements appear. And also the diagram which consists of equivalent points appear.

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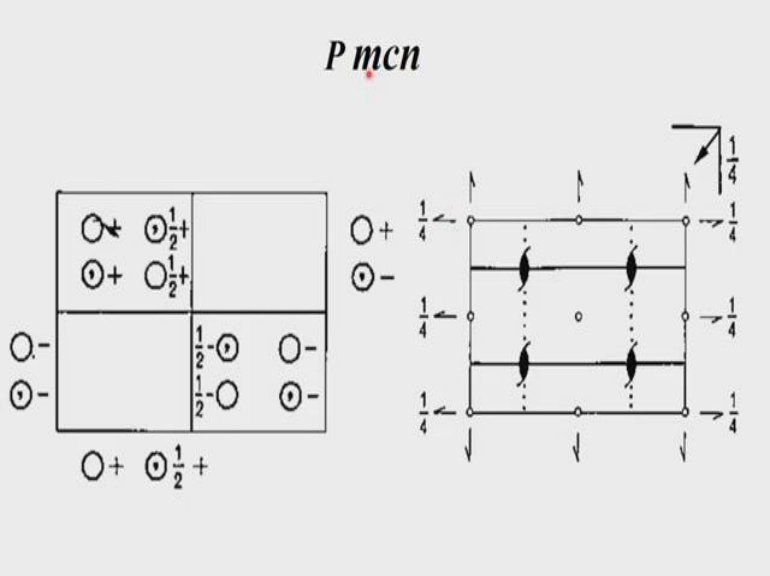

We also discussed the fact that we an orthorhombic system *a b c* can be interchanged. So, depending upon that the corresponding symbols associated with the point group symmetry will also change. And therefore, you know the even though this point group symmetry is here 2/*m* 2/*m* 2/*m* the order in which they come can be not exactly the way in which it is written in the international tables. So, this particular space group, if one structures in the international tables you will not find. However, this is the space group in which the structure of calcium carbonate is reported earlier on. And that is why I thought that I will take this as an example.

The other issue is that we have, we are now in a situation to appreciate the structural aspects associated with the space groups. See we know that we have been discussing that

with respect to objects like here, but instead of objects now we have realistic atoms, which are connected to each other to form a molecule or a compound which is represented in the unit cell and so on. So, since we have come to that kind of a situation, we will now take an example of the structure of calcium carbonate. And it is reported in literature in the space group *Pmcn*. So, we will take into account this space group *Pmcn*.

You are all familiar now with the way in which *P mcn* develops and the way in which the positions of the individual symmetry operations appear in this space group. We know that one once there is a primitive lattice the number of lattice points is 1. The mirror symmetry is now perpendicular to the *a* axis you see that this is the mirror and it is perpendicular to the *a* axis. Remember this is 2/*m* 2/*c* 2/*n* and with our knowledge on the way in which the symmetry element moves away from the origin when we have a translation involved symmetry operations. This actually now represents the mirror at one-fourth along the *a* direction.

So, it moves one-fourth perpendicular, this is the *a* direction it moves one this is the *a* direction sorry, it goes to one one-fourth and then it is normal to the *a* direction. So, the mirror plane is normal to the *a* direction, and it is removed by one-fourth in these direction. Now if we take the *c* glide into account that again moves by one-fourth and this moves now in a direction which is perpendicular to this. we also invoke the presence of additional 2_1 screw axis, as we discussed in the case of *Pbca* additional 2_1 screw axis will develop at various places along the three directions.

The fact that this is a centrosymmetic system, we now put the centre of symmetry at the origin. The moment the system is centrosymmetic we have to put this symmetry centre of symmetry at the origin. So, 000 therefore, is up here, and this is the *a* direction, this is the *b* direction and we have now a mirror plane which is removed by one-fourth and is normal to the *a* direction. A *c* glide removed by one-fourth and is normal to the *b* direction.

And the appearance of the *n* glide is shown up here, because it occurs in the third dimension and therefore, it is shown with a typical symbol which represents the glide plane and this arrow which is coming in the diagonal says that it is the *n* glide. So, we therefore, have the full representation of the mirror, the *c* glide and the *n* glide in this symmetry diagram. So, this is a complete symmetry diagram representing the *P mcn*.

The way in which the equivalent points develop as a consequence are shown here and we will have to refer to the next slide to understand what these positions are.

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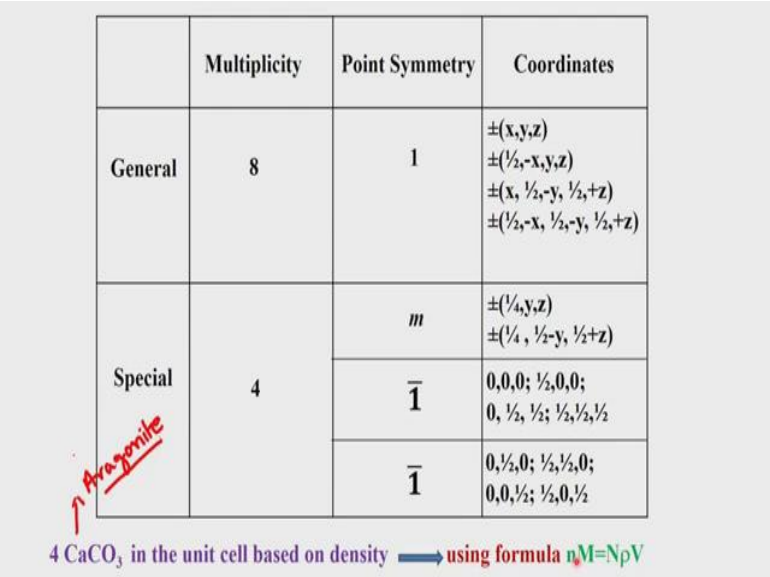

For example, there are 8 possible symmetry positions in the unit cell in the general position. The point symmetry being 1 and those 8 positions are given here.

Since the crystal system is centrosymmetic we have plus x y z and also –x –y –z . So, x y which are now indicated here. Now the presence of the mirror plane which is now at one-fourth will generate the mirror plane is going up here now. And since the mirror plane is going down here in this direction, we see that there is a mirror relationship between these two objects and so, also the mirror relationship between these two objects which are generated due to the presence of the centre of symmetry which exists here.

So, we see that also the presence of these *n* glide and the *c* glide, will introduce these two additional symmetry elements. So, overall we get a mirror symmetry at this position under *c* glide at that position, and so the total number of equal end points after transforming from outside of the unit cell to the inside will give raise to 8 of them. I want you to learn and work out how these equivalent points come based on the table which is given up here, I do not think we have time to discuss that again and again. We have already seen the orthorhombic symmetry we have seen $P\,mc2_1$, we have seen *Pbca* and

we have of course, very clearly seen 2_1 2_1 2_1. So, we have a knowledge of how these equivalent points get generated.

And since the coordinates are given here find out where these coordinates are with respect to the diagram which is shown here. Then you will be convinced that there are 8 equivalent positions corresponding to these 8 general positions. Now the it so happens that in this space group because of the additional possibility of the object having a mirror 1 symmetry that is t 1 symmetry which is again a centre of symmetry. We get special positions. We are quite aware of how these special positions develop.

So, I will not spend time again on this one, except to tell you that there are three possible positions which all generate 4 multiplicity. So, z = 4 which means that in fact, we will have only half the molecular allowed, with respect to the general 8 positions. So, these 1 position 1 position and the total number of equivalent points are 8. Now we come to a situation where we look at the realistic situation.

So, we are now going to take this structure of calcium carbonate, the particular there are various ways in which calcium carbonate crystallizes and one of the ways in which it crystallizes is referred to as the mineral is referred to the mineral phase which is called Aragonite. So, this is a naturally occurring mineral, this mineral aragonite. And the structure of this goes into the space group *P mcn*. The crystal structure has been determined, crystal single crystals of aragonite have been grown in the laboratory the structure has been determined.

Now, the one once the structure has been determined, we get to know the total number of calcium carbonates that are present inside the unit cell depending upon the volume of the unit cell and other factors which I will discuss in a minute. This gives us(Refer time: 08:15) to 4 calcium carbonate that is. So, z is equal to 4. So, there are 4 calcium carbonates units inside the unit cell. That means, the unit cell can accommodate 8 equivalent positions, but it can have only four calciums.

So, since it can have only four calciums, the calcium atoms can be associated with a mirror point symmetry, 1 point symmetry which is with 0 0 1 point symmetry which is with 0 ½ 0. Because all these three possibilities can be taken

into account, and calcium can have a choice where it wants to sit. See this is how the structures develop you see calcium carbonate we already know has certain restrictions from the way in which it forms the structure. The calcium coordination site is the one which decides how the coordination around calcium should develop in the crystal structure.

So, the calcium therefore, since there are only 4 calciums, these four calciums can go to 1 1 , it can take any one of these. And same is the story with the carbon, there are 4 carbon atoms. On the other hand there are 4 times 3, there are 12 oxygen atoms. So, these oxygen atoms have a very clear liberty of how they could arrange in generating the calcium coordination. Because these 12 can be, see 8 of them can be sitting in general position. And 4 can be in any of these three special positions, that is one option. The 1 , 1 and m positions. That will also total up to 12. So, now, is a situation where we have a unit cell which is *P mcn* into which the crystal structure has gone into, calcium carbonate has gone into that structure generating the mineral aragonite which is a naturally occurring mineral.

So, when the naturally occurring mineral formed, these were the options that were given for the compound to form. Calcium, carbon and oxygen these were the options which were given for this thing to form. So, calcium therefore, can have four that can be 4 calciums, 4 carbons and 12 oxygens and as we discussed the distribution among the various types of symmetry elements in the unit cell is possible. Now how do we find out how many molecules are there in the unit cell? that is done by using this formula n M equals N rho V. This formula $n M = N \rho V$.

Let me explain this formula in a little more detail. n is the total number of molecules in the unit cell which could be the z value. M is the molecular weight associated with the compound. Since we know what compound is crystallizing we can have the identification of the molecular weight, we can determine the molecular weight of calcium carbonate by knowing the atomic weight of each one of these atoms and adding them up into the compounds so, we have the molecular weight. We can also determine the molecular weight of this particular crystal using mass spec.

So, we will have a measure of the molecular weight, so experimentally or theoretically we can simply calculate by using the atomic masses. So, we know the molecular weight

of the system. N is the Avogadro number. The Avogadro number is 6.023 into 10 to the power of 23 as most of you know per mole. And that Avogadro number is a constant and it can fix the molecules inside the unit cell. So, N is the Avogadro number. ρ is the density of the crystal. We will talk about the density of the crystal in a little while, ρ is the density of the crystal and V is the volume of the unit cell.

So, in this particular case one once we know the value of *a b* and *c*, this is an orthorhombic system because the crystal system as you see is *P mcn* crystal system is *P mcn*. So, it is an orthorhombic system. In the orthorhombic system the volume will be *a* times *b* times *c*. The product of the three *a, b* and *c*. And therefore, if V = *a*.(*b* x *c*) we can calculate the volume. So, one once we have this volume available to us, which is from the experiment which has been determined to using x-ray diffraction to show that there are four molecules in the unit cell. How do we find out that there are four molecules in the unit cell is what we are discussing now.

So, we first determine the cell dimensions. We determine the value of *a, b, c; α, β, γ* . We identify the space group and this has been identified as *Pmcn*. Then we go ahead and calculate the volume of the unit cell. So, we have volume known in this expression, we know the volume we know the Avogadro number, we know the molecular weight. The two unknowns are the number of molecules in the unit cell and the density associated with the crystal. the density associated with the crystal can be measured. In earlier days as I mentioned in the previous discussion previous class, that we were asked to determine the density whenever we do any crystal structure determination it was a compulsory requirement.

But now people do not bother about it and they simply get whatever density the software gives, they assume that is the density of the crystal. There is always a possibility of going wrong in these in this assumption. Because the software gives the density of the crystal based on the value of M and suppose let us say in this example n was assumed to be 8 then we will get a wrong density. Because we know that n is equal to 4 by eventual determination of the density.

So, how one determines the density of a crystal? The density of a crystal is determined based on an experiment which is known as the flotation experiment. It is basically the principle of Archimedes. You know the principle of Archimedes that when an object is

immersed inside a solution the weight of the object equivalent will be taken out from the liquid, so it will be displaced from the liquid, so the volume of the liquid is equivalent to the weight of the sample which is inside. So, if a person gets into the bathtub as Archimedes did certain amount of water flew from the bathtub and that is how the Archimedes principle came up as you all know.

So, similar thing we assume here. So, what we do is, we take, we roughly take two we take two liquids, one with a lower density and another with a higher density. And these two liquids these two solvents for example, these two solvents could have a property that this compound calcium carbonate will not dissolve in them. So, for example, in this case we cannot take water. It will dissolve in water. So, we have to take two solvents, let us say we take alcohol on one hand and then some higher density liquid which could be methylene bromide or methylene iodide or something like that, these solvents are chosen in such a way that calcium carbonate will not dissolve in them. We already know the densities of these two liquids from literature.

So, we take the value of the literature for these two liquids and then we drop the crystal one single crystal of calcium carbonate is taken and is dropped inside the liquid, in one of the solvents. Let us say we take the solvent which has lower density and then we drop the crystal inside the solution which has lower density than the anticipated density of the crystal. Then what will happen? If you have a lower density and you drop the higher density crystal on top of a lower dense liquid what will happen, will it sink or will it float? What will happen? The density of the liquid is lower. So, will it sink or will it float it will sink.

So, if the density is higher it will float. So, we take the mixture of these two nicely mix them up and then put the crystal and adjust the ratios of these solvents, such that there will be one stage we can visibly see the crystal in between the two. That means, if going at their middle. So, we have these two solutions mixed. So, this crystal will float in the middle. This is known as the flotation technique for determining the density. Then we take that mixed liquid and then measure the density of that using a densitometer. We can use either use a densitometer or use a specific gravity bottle and then use the density determination methodology which is very well known from high school.

So, we determine the density of the crystal. So that means, we have the knowledge of N, we know what N is, what ρ is and what V is. ρ is expressed in grams per cc or kilograms per meter cube. then M is the molecular weight of the material and so we know now V rho N and M, we should be able to determine N. And this is the way in which it has been identified that there are four of calcium carbonate units inside this *Pmcn* units . So, to repeat the whole thing once very quickly, we have the material calcium carbonate the aragonite form that has been crystallized. The crystals have been subjected to x-ray diffraction and the unit cell dimensions have been determined by some technique which we are going to learn in the future.

So, we determine the value of $a, b, c; \alpha, \beta, \gamma$. The value of $a, b, c; \alpha, \beta, \gamma$ tells us that it is an orthorhombic system. We go further and determine the symmetry that is associated with this orthorhombic crystal and we find it is *Pmcn*. The moment we know it is *Pmcn*, we know that this is orthorhombic number one and number two there are 8 general positions and 4 special positions have indicated here. There are 8 general positions 4 special positions 1 symmetry.

Then based on the knowledge of the density which has been measured using this methodology we just described. We know the volume, we know the density and we know the Avogadro number. The right hand side is evaluated and is divided by the value of M which is the molecular weight, and that value will give us the value of n and it turns out to be the value of n is 4 that means, we have four calcium carbonate units in this unit cell.

So, that knowledge is gained. Now we will see when we actually determine the structure. What kind of positions calcium took, what kind of position carbon took and what are the positions oxygen took. As we already discussed there is there are only 4 calcium atoms so obviously, these 4 calcium atoms should sit in one of these special positions. Because 8 positions cannot be generated for 4 calciums, there are only 4 calciums. well it can be generated with half occupancies and so on. But that is unlikely in a very nicely determined structure so, in an ordered calcium carbonate structure like that found in the aragonite mineral. We will have four calcium atoms. So, they have to sit in one of these special positions. And the carbon atoms also should sit in one of these allowed special positions.

Oxygen atom as we discussed again, that 4 times 3 is 12. So, it can sit 8 of them in general position and 4 in one of these special positions. Or all three oxygens can be distributed in these three special positions are summing up to 12. So, 4, 4, 4 that will make it one so these are the possibilities. Now this is decided by the nature of the structure. The coordination around calcium the way in which the carbonate units join together and so on. The bonding comes into the picture here, the nature of the bonding the nature of the coordination site around calcium will now tell us how these calcium carbon and oxygen go into this particular space group. Occupying the special positions are the general positions as we have discussed.

So, here is a situation where we have now landed ourselves into that whenever some crystallization takes place of a material or a compound. The compound can go and behave in such a way that the individual elements now constituting the compound can follow the required multiplicity and the special point symmetry and so on and therefore, their coordinates are kind of predetermined when once they go into the space group.

So, the symmetry therefore, is the key factor here, it drives the elements in this particular compound to go into their respective positions. So, we have seen that this is a *Pmcn* space group. So, there are 8 equivalent points, but when they are in special positions they it becomes 4 and therefore we have the possibility that 4 calciums and 4 carbons will sit only in special positions. Whereas, oxygen has the has the freedom to go either there or sit only here. And let us now look at the solid crystal structure. Because we now have an information that n is definitely 4 from this expression.

Now, so, this is a universal expression, this can be used for any crystalline material. Then once we determine the density, once we determine the unit cell dimensions and volume and if we know the molecular weight we can calculate the number of number possible in the unit cell. Suppose we are looking at a structure whose molecular weight is not known, and it goes into a space group where n is fixed. The number of molecules in the unit cell is fixed, this which probably a very good method to determine molecular weight very accurately.

Nobody uses this method, but one can determine the molecular weight of a given compound by using this formula and this determination of the molecular weight will be extremely accurate because we have the $a, b, c, \alpha, \beta, \gamma$ determined at Angstrom level. So,

the accuracy associated with this molecular weight determination will be very very reliable. But this method is quite expensive to do because we have to number one grow the crystals, number two determine the volume by x-ray diffraction experiments. Determine the density by flotation and then calculate the M value so, it is going to be a tedious one instead one can use the routine methodology that is available for molecular rate determination.

But if the compound is unknown, this is the question which we will come again later as we go to the structure determination part if the compound is unknown we do not know whether it is crystal which I have in my hand is calcium carbonate or not is there a way I can find out that it is calcium carbonate. And that is your approach eventually we want to get to the structure determination protocols. To determine where the atoms are and what those atoms are, and in what way they decide to sit inside the unit cell.

So, in principle we have come to the level of first level understanding of how this compound could be. So suppose you are given an unknown compound and you are has to crystallize you crystallize the compound, but you do not know what are the atoms inside that let us say. You only go to the x-ray diffraction machine and then characterize the given unit cell dimensions. And let us say the scattering is very good the crystal quality is very good you get a volume.

So, you use this volume information, you know the Avogadro number and since there is a good crystal that is formed you can also determine the density. So, the right hand side is available to you, for any compound and the left hand side will the right hand side will also tell you what are the various possible general positions with which we can associate this compound to two and therefore, we know roughly what should be the n value or the z value if all the atoms in this structure are sitting in general positions. of course, if they are sitting in special positions also we know the distribution that is possible.

So, in principle we should be able to determine the molecular weight and in the long run in principle we should be able to identify which item is which by looking at the scattering characteristics the details of the intensity analysis and so on. So, the take home from this discussion long discussion rather, is to say that even if you do not know anything about the structure. If for example, the chemists told you that this is the possible formula and he may be totally wrong. It does not matter to the x ray structure specialist.

So, much that you know once in a in a Jack Dunitz made a comment who is one of the top crystallographers of the world. He made a comment that you know a chemist keeps his compound in a dark room he gropes in the dark he makes the compound and gropes in the dark.

So, it could be any of these structures. So, uses various spectroscopic methods some other methods to sort of apriori predict what could be this structure. But this is like entering a dark room and trying to let us say find this monitor inside the dark room, suppose everything is dark here, and we enter the room and we want to find where this is it is going to be difficult.

So, what crystallography does? What crystal structure determination protocol does? In fact, in general what crystallographers do is to come and switch on the light. So, the moment we switch on the light we know where the object is, where the crystal is, where the atoms are, where the atoms are going into the various parts of the unit cell and so on. So, a chemist groups in the dark and the crystallographer gets in and puts on the light in that particular room to find the object.

So, thereby the determination of the crystal structure by x-ray diffraction is unambiguous. One once you do a thorough job of analyzing the x-ray structure then, whatever you have determined is going to be the final structure in the solid state. So, when once you dissolve the crystal in or allow the crystal to become a liquid and liquid becomes gas and so on. The it is not guaranteed that the structure which is in the solid state will be maintained.

Because as you all know the structure in the solid state is such that the molecules are connected to each other by various intermolecular interactions. And these intermolecular interactions could be strong they can be weak depending upon the situation. The molecules arrange themselves to go into a given space group, as we discussed the other day the possibility of polymorphism. They can go into different space groups.

When they go into different space groups different types of intermolecular interactions will hold the molecule together. And as a result one once we disturb these intermolecular interactions we do not know what kind of reorientation occur in the molecule. To a very large extent most of these structures remain unaltered which is, because of the fact that

they are all bound by very strong covalent ionic that kind of bonds, which are strong bonds.

So, energetically it is very difficult to disturb the molecule just by removing the intermolecular interactions. But then there are possibilities particularly in organic systems and so on, where there is a potential for intra molecular interactions to develop in you of the intermolecular interactions. Then you have a possibility that confirmations may change.

So, the conformation you may get from NMR may not agree with the conformation you got from the crystal structure. This is particularly true with small molecules. The story with large molecules particularly proteins and viruses and so on, is very interesting because these molecules they do not crystallize with the intention of having only the molecular species. They always crystallize with a large amount of what we call as solvent water. And there is a lot of water around it. So, more or less the crystal structure if we determine the crystal structure of a protein it mimics the actual structure of the protein in the in the biological media and that is a very big advantage as far as protein structure determination is concerned.

The protein structure also has a issue that it depends upon the various states of salvation. So, you can have polymorphism in proteins as well, depending upon the nature of the salvation dynamics which occurs around the protein molecule and the way in which the solvent structure develops around the protein molecule. Now why we why are we discussing all these issues? We are discussing all these issues to bring home the importance of understanding where the atoms are, and how the atoms now are distributed inside the unit cell.

So, if we consider therefore, the case of this calcium carbonate it crystallizes in a *Pmcn* space group the options that are given to the atoms have already been discussed. So, now, we have to see how the atoms are located. The moment we know how the atoms are located we will know about the geometry of that particular molecule as well.

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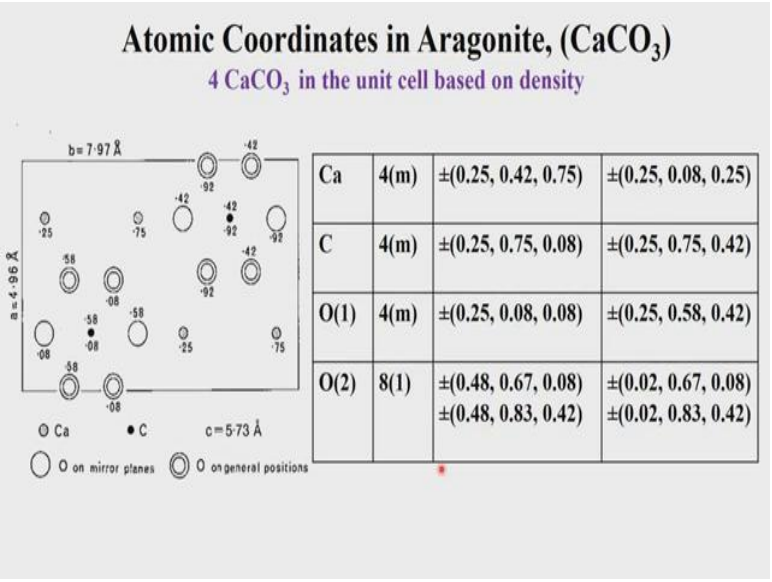

Ca	4(m)	±(0.25, 0.42, 0.75)	±(0.25, 0.08, 0.25)
C	4(m)	±(0.25, 0.75, 0.08)	±(0.25, 0.75, 0.42)
O(1)	4(m)	±(0.25, 0.08, 0.08)	±(0.25, 0.58, 0.42)
O(2)	8(1)	±(0.48, 0.67, 0.08) ±(0.48, 0.83, 0.42)	±(0.02, 0.67, 0.08) ±(0.02, 0.83, 0.42)

So, all these issues will come up if we go to the next slide. And that particular slide will tell you how the atoms in calcium carbonate are actually located inside the unit cell. And we will discuss that in a little more detail. But at this particular moment we see that there are 4 calcium carbonate atoms in the unit cell based on the density. And the atomic coordinates are given in this table, the atomic coordinates tell us that calcium there are 4 calcium atoms the calcium atoms decide to sit in the mirror symmetry position, which is generating the special 4 positions. z equals 4. z equals 4 generation position.

So, we will have therefore 4 calcium atoms. Carbon also decides to use the mirror 1 . But it uses the mirror symmetry 4 of the oxygens use the mirror symmetry. So, this now determines the geometry of the calcium surroundings. And then we have of course, the oxygen to the second one generally occupies all general positions. And at this stage we will discuss independently how we go about understanding this ok.