**Symmetry and Structure in the Solid State**
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**Lecture – 28**
**Crystal Structure of Some Minerals**

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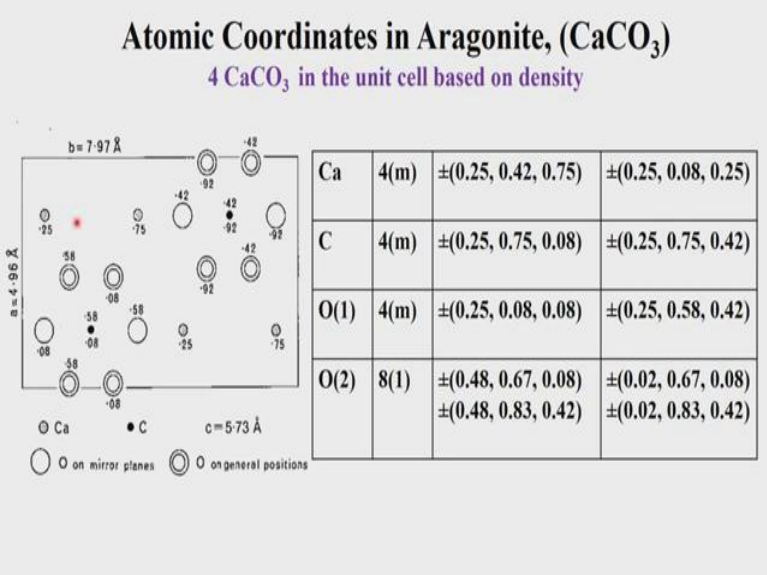


| | | | |
|---|---|---|---|
| Ca | 4(m) | ±(0.25, 0.42, 0.75) | ±(0.25, 0.08, 0.25) |
| C | 4(m) | ±(0.25, 0.75, 0.08) | ±(0.25, 0.75, 0.42) |
| O(1) | 4(m) | ±(0.25, 0.08, 0.08) | ±(0.25, 0.58, 0.42) |
| O(2) | 8(1) | ±(0.48, 0.67, 0.08)<br>±(0.48, 0.83, 0.42) | ±(0.02, 0.67, 0.08)<br>±(0.02, 0.83,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

Let us see now the structure of aragonite in the space group *P m c n*. There are 4 calcium carbonate units in the unit cell. So, we now based on the density it has been determined there are 4 calciums, 4 carbons and 12 oxygen atoms.

When the actual structure is determined these are the cell dimensions *a* is 4.96 Å *b* is 7.97 Å; so, this is now the *a* direction this is the *b* direction. Remember that there is a mirror symmetry at ¼ along this direction and then there is a *c* glide symmetry which is associated in this direction please note that.

So, both those are the mirror symmetry positions. So, we have *ab* projection we have the *c* value as 5.73. So, *a* . (*b* * *c*) will give you the volume of the unit cell from which we can determine the density as we discussed before. So, you see that the calcium atoms sit down the 4 *m* position; corresponding to the *x* value of ± 0.25 and the value of this *z* is 0.75, but what is more important is that they sit at on the mirror which is at ± 0.25. This

is the mirror which is now perpendicular to the *a* axis and so this sits now along the mirror plane.

So, you see that there is one at 0.25 and there is one at 0.75 and these are the calcium positions. So, the additional calcium positions will appear automatically in the space group *P m c n* at these 2 positions; so, we have therefore, 1, 2, 3, and 4.

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| | Multiplicity | Point Symmetry | Coordinates |
|---|---|---|---|
| General | 8 | 1 | ±(x,y,z)<br>±(½,-x,y,z)<br>±(x, ½,-y, ½,+z)<br>±(½,-x, ½,-y, ½,+z) |
| Special | 4 | *m* | ±(¼,y,z)<br>±(¼ , ½-y, ½+z) |
| | | $\bar{1}$ | 0,0,0; ½,0,0;<br>0, ½, ½; ½,½,½ |
| | | $\bar{1}$ | 0,½,0; ½,½,0;<br>0,0,½; ½,0,½ |

1 Aragonite

4 $CaCO_3$ in the unit cell based on density ⟹ using formula nM=NρV

Let us go back and check the mirror symmetry this comes at ±(¼ y z) and we see ± (¼ ½ - y ½ + z) notice that this is ½ - y ½ + z at ¼ again.

So, the positions of calcium are at 0.25, 0.75, 0.25, 0.75 this is now coming at the value - 0.25. So, this one is + 0.25 this is - 0.25 will be also equal to 0.75 by translation. So, for example, if you take this atom onto the - 0.25; it is up there you translate it by one unit translated by this unit you will get back to the 0.25.

So, therefore, we have 1, 2, 3, 4 calcium positions; the carbon positions now sit at ± 0.25 the same mirror. So, we know that there is a mirror perpendicular to the *a* direction, there is a *c* glide which is perpendicular to the *b* direction and *n* glide is coming up with respect to the *c* direction. So, we therefore, see here that the carbon atom also occupies the mirror symmetry 4 equivalent points; that is ± (0.25 0.75 0.08); that means, that the carbon atoms which are shown here appear at 0.08 and 0.58 respectively because this ½ - *z* or ½ + *z* will account for the value of 0.58.

So, I want you to check the what you should do it as a homework is to see take these coordinates and see whether they satisfy the symmetry requirements associated with this 4 *m* position. Then you will convince yourself that calcium carbon are sitting in these special positions. It so happens that the oxygen atom will also sit with respect to ± 0.25 as is shown here in this diagram. So, therefore, these occur at 0.08 and 0.08; you see that the oxygen positions are indicated in a bigger open circle which is shown up here.

So, the carbon atoms came here. So, happens the 2 carbon atoms sit on top of each other this is at -0.08 and 0.58 and the carbon atoms here therefore, are ½ added to the z value. So, they sit at 0.42 and 0.92. And these two values therefore, this is 0.92 is 1 minus 0.08; and this value is 1 minus 0.58.

So, you see carbon atoms come up these positions. So, the carbon is one above the other along the *z* direction; similarly the carbon is one above the other in the *z* direction and the values of calcium are given here they give rise to these 4 positions. So, 4 calcium positions are taken care of 4 carbon positions are taken care of, 4 oxygen positions are represented by 0.08 and 0.48, but the positions of *x* and *y* are different *x* and *y* are different; that means, that we have now a coordination around the calcium atoms located in such a way that we do have the connectivity between carbon and oxygen and then that connectivity now defines the calcium carbonate structure.

So, you therefore, have 8 general positions which are occupied by the second oxygen set and the coordinates are given here and they are represented in this projection. Now this is a projection diagram; now over the last few classes you have realized the fact that even though we represent everything in 2 dimensions eventually the structure is 3 dimensional.

So, here is a challenge for you; it will not be given as an assignment or an examination, but I want you to generate the 3 dimensional structure of calcium carbonate by yourself as a home assignment may be; to find out what is the coordination around calcium. How the coordination develops around calcium and what are the connectivity's in the structure of calcium carbonate by based on the diagram which is given here. If you could work that out then you have become experts in analyzing structures; even before you go and determine the structures using X ray diffraction or any other techniques neutron, electron and so on.

So, effectively what is represented here is a realistic structure; the realistic structure going into the orthorhombic system *P m c n* with 4 of those calcium carbonate units in the unit cell and the way in which the atoms are distributed in the unit cell. So, the calcium carbon and one set of oxygen's all occupy the 4 *m* position and the 8 *i* position which is the general position is occupied by 8 oxygen atoms. So, totally we have 12 oxygen atoms 4 and 4 calcium and carbon and this determines the entire structure in the unit cell.

So, what are the assumptions we have made here? We have made the following assumptions; we have assumed that we know the structure; we have assumed that we have done at X ray diffraction experiments which we will do later and we have assumed that we know the unit cell dimensions and then the density; so that we know that there are 4 molecules in the calcium carbonate structure. So, these are the things which one has to do.

So, this is of course, as they say it is better to think before you do the experiment we are now thinking before doing the experiment. And this is in terms of where the atoms are coming and where they are sitting with respect to the known calcium carbonate structure. So, if we know the structure yes we can definitely think about it and determine the 3 dimensional structure right. So, this now takes us to the possibility of looking at many structures which are already known. This is not our ambition anyway we want to find out methodologies to determine the structures in the long run.

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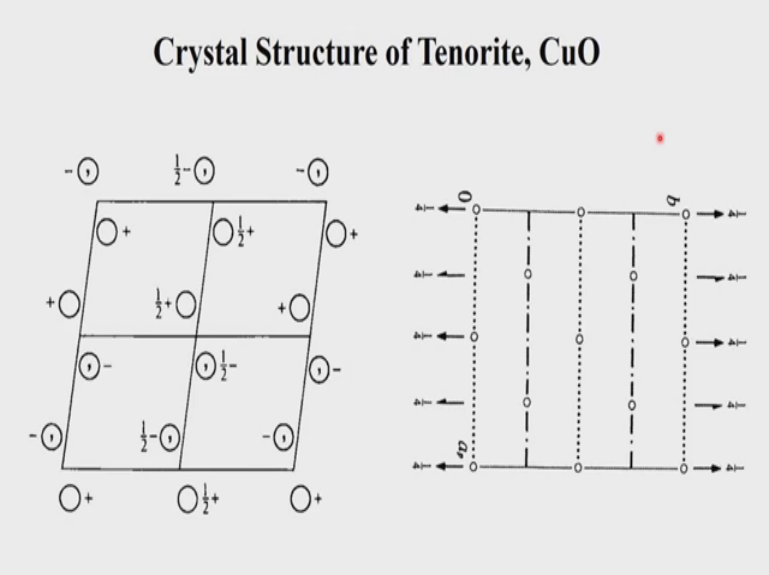


But we will look at one more which is the very simple structure of copper oxide. Copper oxide goes into the is another mineral called tenorite and this is the structure of copper oxide.

This tenorite structure crystallizes in this space group, I want you to find out what is this space group. By looking at the equivalent points and also looking at the *ab* projection which is shown here; what do you think is the system. You have for example, lot of ½ ½ ½ ½ indicated here and you also see that this angle is $\beta$. So, the structure has to be $a \neq b \neq c$ and $\beta$ is $90^0$. What is the system?

It is a monoclinic system and in this monoclinic system we have lot of ½ ½ ½ coming up and therefore, it has to be a *C* centered lattice. We see here in this diagram if we now carefully look at this particular diagram we get a *c* glide which is associated with the origin *O* here. So, and then we also get a twofold associated with that origin. So, there is a *c* glide and a twofold intersecting with respect to each other with a 2/*m* symmetry. So, it is a centro symmetric monoclinic system apart from that we also have the fact that these 2 and *c* are intersecting at this origin.

So, it has to be this space group *C* 2/*c*. So, we have inferred that the copper oxide tenorite goes into the space group *C* 2/*c*; *C* 2/*c* boasts itself of 8 equivalent positions right.

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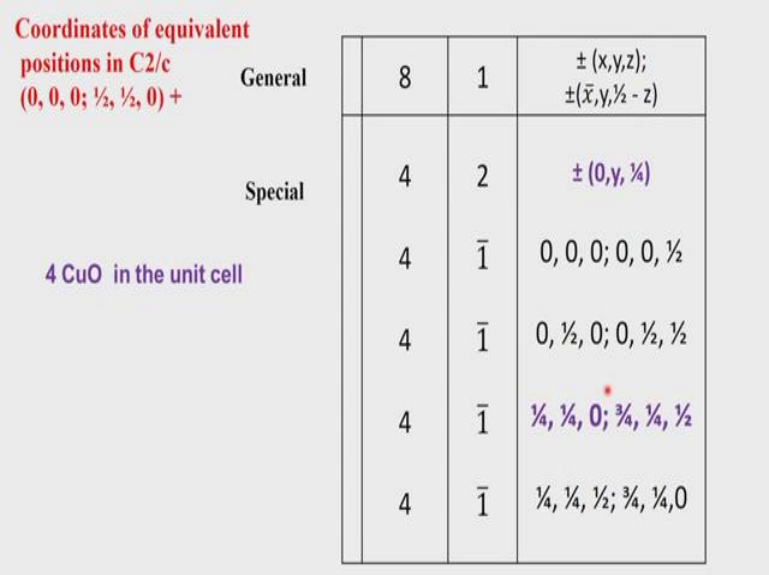


| | | | |
|---|---|---|---|
| General | 8 | 1 | ± (x,y,z); ±(x̄,y,½ - z) |
| Special | 4 | 2 | ± (0,y, ¼) |
| | 4 | $\bar{1}$ | 0, 0, 0; 0, 0, ½ |
| | 4 | $\bar{1}$ | 0, ½, 0; 0, ½, ½ |
| | 4 | $\bar{1}$ | ¼, ¼, 0; ¾, ¼, ½ |
| | 4 | $\bar{1}$ | ¼, ¼, ½; ¾, ¼,0 |

So, we will list those 8 equivalent positions; those equivalent positions are generated by ± *x y z*; ± *y* ½ - *z* I think 4 there are two more sets which was missing in this in this table; we will have to add that up ± *x y z*, ± y ½ - z; what is missing is the addition of ½ ½ 0 to these 4.

So, it is not purposely missed it is not shown here the; what is shown here is with respect to 0 0 0. So, there are 4 equivalent points corresponding to 0 0 0; 4 other equivalent points corresponding to the addition of ½ ½ ½. It has several special positions; now the several special positions sorry the several special positions can be of symmetry $\bar{1}$ or of symmetry 2; 2 possibilities again exist. Just like we saw the *P m c n* case where we had $\bar{1}$ and the mirror symmetry in the previous case; we had the position of $\bar{1}$ available, but all the atoms decided to occupy the mirror symmetry.

So, here we have four $\bar{1}$ positions that are available and these are the corresponding coordinates; you will have to generate the additional coordinates. Here only two are given; that means, you have to add ½ ½ 0 to each one of these to get to the 4 equivalent points. So, we know where the equivalent points are, we have very clearly and quietly determined that this space group is *C* 2/*c* without having any information earlier.

So, this is $C\,2/c$ and then there are these distribution of equivalent points. Now what we will have to see is how many at how many units of CuO are in the unit cell. So, we have to go ahead and determine the unit cell dimensions; we will determine the $a\ b\ c$ and we know a $\beta$ is non $90^{o}$; so, we have to determine the $\beta$ value also.

So, one once we determine $a\ b\ c\ \beta$ we have the unit cell dimensions. So, we can calculate the volume of the unit cell; we can measure the density of CuO just like we did the density of calcium carbonate in the previous example; so we know the density. Avogadro number is known and then of course, with copper oxide given to you we know the molecular weight. And it turns out that if we use the formula $Z * M = N \rho V$; we will end up with 4 copper oxide units in the unit cell.

So, therefore, we can if you want to call it a molecule it is not really a molecule; it is a compound. So, 4 CuO units in the unit cell; so the this means to say that the choices are again clear and very very clear because nothing is in the general position in this structure because anything in the general position will generate 8 equivalent points. So, we already know that this is not occupied at all. So, general positions we can forget about; even though we have the option of having the general positions, this particular compound decides to sit in only special positions.

Now; that means, to say that this will now have the choice of 5 different possibilities; it can sit the copper atom can sit in this position this position this and that and so also oxygen. There is only 1 copper and 1 oxygen is a much simpler example than calcium carbonate. So, both the atoms have no choice, but to sit in special positions in the unit cell. So, the atoms now, therefore, have to sit in special positions; so we now go and see the structure.

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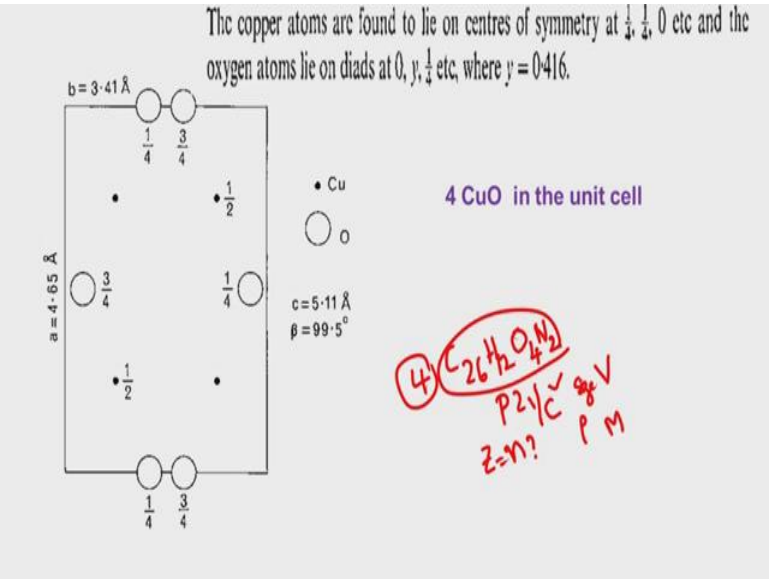


If we go and see the structure we see that the copper atoms are found to lie at centers of symmetry; which is ¼ ¼ and 0; that means, it corresponds to ¼ ¼ 0.

So, this are highlighted it here; the highlighted one is the place where the copper atoms decide to occupy. The oxygen atoms likewise decide to occupy the twofold symmetry; the twofold symmetry which also generates 4 equivalent points. So, the oxygen atoms decide to go and sit there the copper atoms decide to sit here. And so you get this structure which is written here 4 copper atom CuO in the unit cell; the oxygen atoms lie at 0 *y* ¼; the value of *y* being 0.416; remember this is a *C* 2/*c* space group; so, the origin is fixed.

So, now the choice of fixing the *y* is not independent; you see you have a twofold axis alone then the *y* axis is arbitrary where we fix the *y* value is arbitrary. But when once we have a centered system like 2/*m* point group symmetry here the origin is fixed at 0 0 0. So, the value of *y* therefore, is coming at 0.416 when you determine the structure. So, the crystal structure has been determined *a* is 4.65, *b* is 3.41; *c* is 5.11 and $\beta$ is 99.5.

So, this gives rise to our unit cell and therefore, we can calculate the volume the volume of the unit cell in turn will allow us to calculate the number of molecules; in the unit cell there are 4 CuO units in the unit cell. The positions of the atoms are marked in this projection again the projection down *a* and *b*. So, *c* axis is coming perpendicular; so therefore, this angle is 90°.

The *c* angle is coming in *a* direction which forms the angle $\beta$ 99.5. So, you see therefore, the copper atoms sit at this and that position because they want to occupy the ¼ along *a* and ¼ along *b* and 0 along *z*. So, one once they come there the *C* 2/*c* operation the will ensure this presence of the center of the *C* centering will ensure that if we get an object at ½ .

And again that ½ is repeated here through the center of symmetry which is present at this ½ position ½ along *x* ½ along *y* and therefore, that will generate this ½ and this one; so, the positions of the copper atoms are fixed. The oxygen atoms on the other hand occupy the value of y equals 0.416. So, if the copper atom is at ¼ ¼ 0 that is 0.25,0.25 and 0.

And then this oxygen atom comes at 0.25, 0 y and ¼; that means, the value of *z* is 0.25 and the value of *y* is 0.4. So, we can have the coordinates of this atom at ¼ ¼ 0; coordinates of this atom are at 0, 0.416 and ¼ that is 0.25. Since we know the cell dimensions these are the fraction coordinates which I am talking about. So, ¼ ¼ 0 is the position of copper; then the 0, 0.416 and ¼ are the positions of the oxygen atom.

So, we can calculate the length bond length between copper and oxygen; I want you to do this again. Remember we are in a monoclinic system; so you cannot just directly measure the distance between these two and say it is the bond length; you have to calculate the bond length the value of $\beta$ comes into the picture and so there will be a sin $\beta$ component which will come in your calculation.

So, one can calculate therefore, the bond distance between them. So, the geometry of copper oxide can easily be calculated; either this geometry with respect to that or that geometry or that geometry. Again remember that they are all gone by the *C* 2/*c* symmetry. So, the symmetry will now allow only these possible positions for the axis in atom. So, in a nutshell we have seen two structures; two independent structures and we have seen the space groups into which they can go by based upon the symmetry diagrams and also the equivalent point diagrams.

And we have determined the crystal structure particulars particularly the crystal structural details *a b c*, $\alpha\ \beta\ \gamma$ and from that we have inferred the possible space group. So, we know the space group we know the positions of the atoms where the space groups allow the atom positions. So, all the allowed atom positions are identified with respect to the molecule which we want to put into that.

For example, in the case of the copper oxide we want we can put this into 8 equivalent points if they are all in general positions and 4 equivalent points if they are in special positions. What we then determine is the density of the crystal one once we determine the density of the crystal; they we will have 4 copper oxide units indicated. And there moment we have 4 copper oxides indicated we know that there are no general position occupation in this particular structure.

So, this way we can determine the structure. So, what are all the things we know how to determine the we need to know to determine the structure? We need to know what is the molecule ,we need to know how the atoms are positioned with respect to the unit cell, we need to know whether how many special positions get occupied and how many positions general positions get occupied and so on. So, suppose you have a structure like this let me draw it suppose you have a structure which is let us say at C26 H12 is a hypothetical structure O4 N2 and let us say this structure goes into a space group $P\,2_1/c$ by $a\ b\ c\ \alpha\ \beta\ \gamma$ we find out it goes into $P\,2_1/c$; this is fine.

Now, we also know the positions of the special positions unit cell where the size of the unit cell we know. So, the size of the unit cell we know. So, we know the volume; we know the volume we can also measure the density. So, we know the density and since somebody said this is the molecular formula then we can calculate the molecular weight; so, M is known P $2_1/c$.

So, I can calculate the number of molecules in other words the value of Z or the number of molecules what is the value of n we can calculate.

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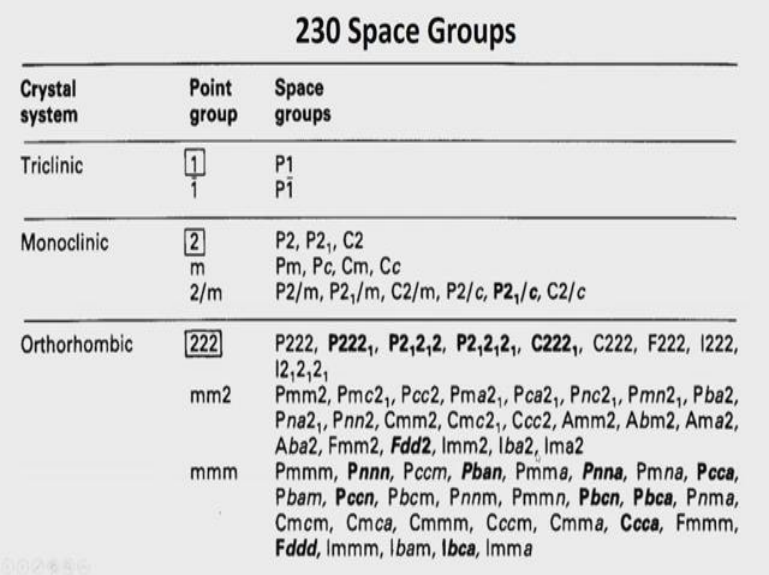

**230 Space Groups**

| Crystal system | Point group | Space groups |
|---|---|---|
| Triclinic | 1 | P1 |
| | $\bar{1}$ | $P\bar{1}$ |
| Monoclinic | 2 | P2, $P2_1$, C2 |
| | m | Pm, Pc, Cm, Cc |
| | 2/m | P2/m, $P2_1/m$, C2/m, P2/c, $\mathbf{P2_1/c}$, C2/c |
| Orthorhombic | 222 | P222, $\mathbf{P222_1}$, $\mathbf{P2_12_12}$, $\mathbf{P2_12_12_1}$, $\mathbf{C222_1}$, C222, F222, I222, $I2_12_12_1$ |
| | mm2 | Pmm2, $Pmc2_1$, Pcc2, $Pma2_1$, $Pca2_1$, $Pnc2_1$, $Pmn2_1$, Pba2, $Pna2_1$, Pnn2, Cmm2, $Cmc2_1$, Ccc2, Amm2, Abm2, Ama2, Aba2, Fmm2, **Fdd2**, Imm2, Iba2, Ima2 |
| | mmm | Pmmm, **Pnnn**, Pccm, **Pban**, Pmma, **Pnna**, Pmna, **Pcca**, Pbam, **Pccn**, Pbcm, Pnnm, Pmmn, **Pbcn**, **Pbca**, Pnma, Cmcm, Cmca, Cmmm, Cccm, Cmma, **Ccca**, Fmmm, **Fddd**, Immm, Ibam, **Ibca**, Imma |

So, having calculated the value of n; I would like to see whether I can determine the structure see the complexity which is associated with the structure. So, far what we saw was copper and oxygen right and we also found that by density calculations there are 4 molecules in the unit cell.

Suppose this also by density tells us that there are 4 molecules in the unit cell then there are 4 general positions in $P\ 2_1/c$. So, we therefore, have to determine 26 positions of carbon 16 positions of oxygen 8 positions of nitrogen and 12 times 4; 48 positions where hydrogen can sit. Now is it practically possible to follow this methodology which we have discussed so far to determine the structure of this? Obviously, not; so the structure determination therefore, is not so very straight forward.

We have taken two examples where we already know the structure and so we are talking about where they are sitting. In these cases we do not know where the atoms are going to sit 4 general positions; 26, 12, 4 and 2 atoms have to be distributed we do not know the structure of how these atoms are connected to each other and so on.

Therefore we have to do the structure determination and there we use the X rays X ray diffraction as a technique to determine this and we will see how we do that in the coming classes. Now we have seen the structure of calcium carbonate and copper oxide which are two simple examples. Just to illustrate the reality of our the fact that the information

about the space group, the information about the possibility of general and special positions is a must.

Even otherwise if we know the structure we can fix where the atoms are if we do not know the structure also, we have to have this information before we go on determine make an attempt to determine the structure. And that is where the whole thing boils down to; the whole thing boils down to the fact that we need to therefore, have an idea of what the space group into which the crystals is not they evolve it into which the compound goes into.

This is a simple example suppose you take a protein there will be hundreds of atoms; now these hundreds of atoms suppose the protein let us say is crystallizing in a space group we will see what are all the possible space groups into which proteins can crystallize. We will see that the number of space groups will not be 230, but it will reduce we will see it in a few minutes, but the fact remains that we should know the space group information.

So, when we do the X ray diffraction experiment we will find the unit cell dimensions we will also have to find out a method by means of which we can find the space group information. Remember the space group information is built in through the symmetry and we have we are able to identify what are all the symmetries that are present. Now what the presence of symmetry does to X ray diffraction is something which we have not studied right. So, what the symmetry does to the X ray diffraction is the next step and that we will study in the coming classes.

So, at this moment we now have a understanding of the nature of the space group. So, now, we can list out the 230 space groups straight away instead of going into the individual details we have. In fact, examined the triclinic system thoroughly it can go into 1 and $\bar{1}$ the point group symmetries and the space groups are *P* 1 and *P* $\bar{1}$. In fact, we have systematically analyzed also the monoclinic system where the point of symmetries are 2, *m* and 2/*m*.

So, using the monoclinic point group symmetry we can construct the possible space groups you have taken examples of *P* 2, *P* $2_1$ and *C* 2. And we have taken examples of *P* *m* and *C* *m* we have shown also *C* *c*. So, we have therefore, in a monoclinic system 1 2 3

4 5 6 7 8 9 10 11 12 13; 13 possible space groups that can go into this system and we also showed in this case that the other there are no other possibilities; other than these possible space groups. So, 13+2; so 15 space groups have been generated; when once we come to the case of orthorhombic symmetry we have 3 point group symmetries 2 2 2, *m m* 2 and *m m m.*

Now, here you see that there are so many possibilities because we have different lattices which can come in. You see in the case of the monoclinic system we had a primitive lattice under *C* centered lattice no other possibilities. This is in fact, we have not shown that, but maybe you can (Refer Time: 25:38) in a in a one of the one of the TA session we can show that that the primitive the *C* centered lattice can also be *I* centered and things like that. And if we there is a *B* centered lattice it will go itself into a primitive lattice this can be shown in a TA example.

So, the number of space groups therefore, are limited in case of the monoclinic system. Because the number of lattice symmetries are lattice types are *P* and *C* only whereas, orthorhombic has all possible lattices. So, it has the primitive lattice generating so many of these possible space groups we have discussed $2_12_12$ and $2_12_12_1$ in great detail. We can also have a crystal system the with a space group *C* 2 2 $2_1$; *C* centered lattice, we can have a face centered lattice and a body centered lattice and of course, *I* $2_12_12_1$ is also possible.

If we take the point group symmetry *m m* 2 we took some examples and we studied in fact, I think one of these *P c a* $2_1$ is this is this space group we studied in detail, but you see the number of point space groups to which it can belong to.

So, there is a plethora of possibilities with *m m* 2 symmetry and more possibilities with *m m m* symmetry; *m m m* remember is 2/*m* 2/*m* 2/*m*. So, this is the possible number of centro symmetric space groups in the orthorhombic symmetry. The number of centro symmetric space group in the monoclinic symmetry is corresponding to this point group 2/*m* or these and the number that is possible in triclinic with centro symmetry is that.

So, the centro symmetric crystals therefore, can generate only these many space groups though the other space groups which are shown here or do not have inversion centers. So, this brings us the restriction on the way in which crystallization can occur. The crystallization can occur either to generate centro symmetric systems or non-centro

symmetric systems and it is of importance to note that if everything is centro symmetric, the properties as described by that material is not very exciting.

In fact, the center of symmetry is a consequence of a little more perfect arrangement than in the case of a non centric symmetry the very fact that we say centro symmetric and non-centro symmetric is in that context. So, if the space groups to which it goes into are non-centro symmetric; the possibility of anisotropic properties which might develop in different directions are many more. So, the non-centro symmetric crystals are more exciting and more important than these centro symmetric structures; even though centro symmetric structures are necessary to get an understanding of the isotropic nature of given materials.

So, the if a material displaces particular property along some direction; it is generally the case with non-centro symmetric space groups than centro symmetric space groups.

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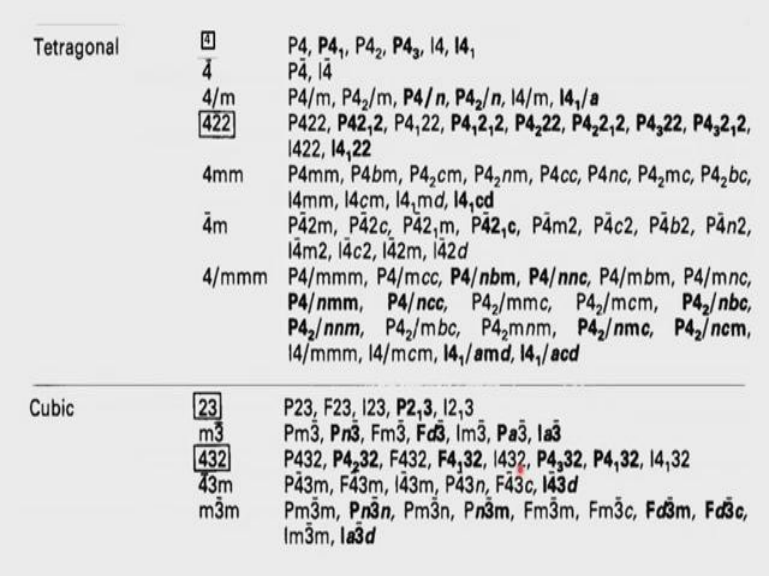

| | | |
|---|---|---|
| Tetragonal | 4 | P4, **P4$_1$**, P4$_2$, **P4$_3$**, I4, **I4$_1$** |
| | $\bar{4}$ | P$\bar{4}$, I$\bar{4}$ |
| | 4/m | P4/m, P4$_2$/m, **P4/*n***, **P4$_2$/*n***, I4/m, **I4$_1$/*a*** |
| | 422 | P422, **P42$_1$2**, P4$_1$22, **P4$_1$2$_1$2**, **P4$_2$22**, **P4$_2$2$_1$2**, **P4$_3$22**, **P4$_3$2$_1$2**, I422, **I4$_1$22** |
| | 4mm | P4mm, P4*bm*, P4$_2$*cm*, P4$_2$*nm*, P4*cc*, P4*nc*, P4$_2$*mc*, P4$_2$*bc*, I4mm, I4*cm*, I4$_1$*md*, **I4$_1$*cd*** |
| | $\bar{4}$m | P$\bar{4}$2m, P$\bar{4}$2*c*, P$\bar{4}$2$_1$*m*, **P$\bar{4}$2$_1$*c***, P$\bar{4}$m2, P$\bar{4}$*c*2, P$\bar{4}$*b*2, P$\bar{4}$*n*2, I$\bar{4}$m2, I$\bar{4}$*c*2, I$\bar{4}$2*m*, I$\bar{4}$2*d* |
| | 4/mmm | P4/mmm, P4/*mcc*, **P4/*nbm***, **P4/*nnc***, P4/*mbm*, P4/*mnc*, **P4/*nmm***, **P4/*ncc***, P4$_2$/mmc, P4$_2$/mcm, **P4$_2$/*nbc***, **P4$_2$/*nnm***, P4$_2$/*mbc*, P4$_2$*mnm*, **P4$_2$/*nmc***, **P4$_2$/*ncm***, I4/mmm, I4/mcm, **I4$_1$/*amd***, **I4$_1$/*acd*** |
| Cubic | 23 | P23, F23, I23, **P2$_1$3**, I2$_1$3 |
| | m$\bar{3}$ | Pm$\bar{3}$, **Pn$\bar{3}$**, Fm$\bar{3}$, **Fd$\bar{3}$**, Im$\bar{3}$, **Pa$\bar{3}$**, **Ia$\bar{3}$** |
| | 432 | P432, **P4$_2$32**, F432, **F4$_1$32**, I432, **P4$_3$32**, **P4$_1$32**, I4$_1$32 |
| | $\bar{4}$3m | P$\bar{4}$3m, F$\bar{4}$3m, I$\bar{4}$3m, P$\bar{4}$3*n*, F$\bar{4}$3*c*, **I$\bar{4}$3*d*** |
| | m$\bar{3}$m | Pm$\bar{3}$m, **Pn$\bar{3}$*n***, Pm$\bar{3}$n, **Pn$\bar{3}$m**, Fm$\bar{3}$m, Fm$\bar{3}$*c*, **Fd$\bar{3}$m**, **Fd$\bar{3}$*c***, Im$\bar{3}$m, **Ia$\bar{3}$*d*** |

Now, what we will do is we will go and finish off this table; you see when we got a tetragonal you get enormous number of space groups. I want you to find out which of these are centro symmetric of course, now we are experts in these areas there is a fourfold symmetry which is of course; obviously, non-centro symmetric $\bar{4}$ is non-centro symmetric. I wanted to find out your 4/*m* is centro symmetric and is 4/*m* centro symmetric; we have to see $\bar{4}$ is it centro symmetric or non-centro symmetric.

So, these are issues which come up; in fact, $\bar{4}$ could be centro symmetric because $\bar{4}$ has a property where you have the 4 fold along with the repetition of the centro of symmetry associated with it. It is just like $\bar{2}$ is equal to mirror what is $\bar{4}$? So, these are questions which I leave unanswered so that you will make some mental calculations about which is centro symmetric which is and non-centro symmetric and so on. And therefore, in this case you have therefore, the point group symmetries are more and there is also these possible space groups.

What is very important to notice here is that in case of the tetragonal system because $a \neq b$ the basal plane is square. And because it is square the centering of that particular square alone is not possible and at the same time if the base is squared then the other 2 perpendicular directions are independent of each other. And therefore, the only possibility of having the other than a primitive lattice for the tetragonal system is the body center.

So, for a tetragonal system we will not get the face centered space groups or the *A* or *B* or *C* centered space groups because of the fact that a = b, but that decides that we cannot have this and this is the case which we should remember. On the other hand if we go to the cubic system now the cubic system has several point group symmetries and cubic is unique because we have $a = b = c$, $\alpha\ \beta\ \gamma$ are $90^{o}$.

The only clear cut symmetry that has to be and must be present in a cubic system is the threefold symmetry and that should be along the diagonal. If you see the threefold symmetry here 3 $\bar{3}$ 3 3 and $\bar{3}$ all these symmetries are along the 1 1 1 crystallographic direction. So, by 1 1 we will soon understand and try to see how these crystallographic directions crystallographic planes and things like that develop when we now try to understand the internal symmetry associated with the unit cells which we have not touched upon so far.

What we have done is the internal symmetry with respect to these point groups and the space group distributions; the generation of equivalent points. We have taken 2 realistic examples and see where the atoms are and so on. But how do we identify the position of the atom with respect to the internal structure of the unit cell is something which we will study in a near future.

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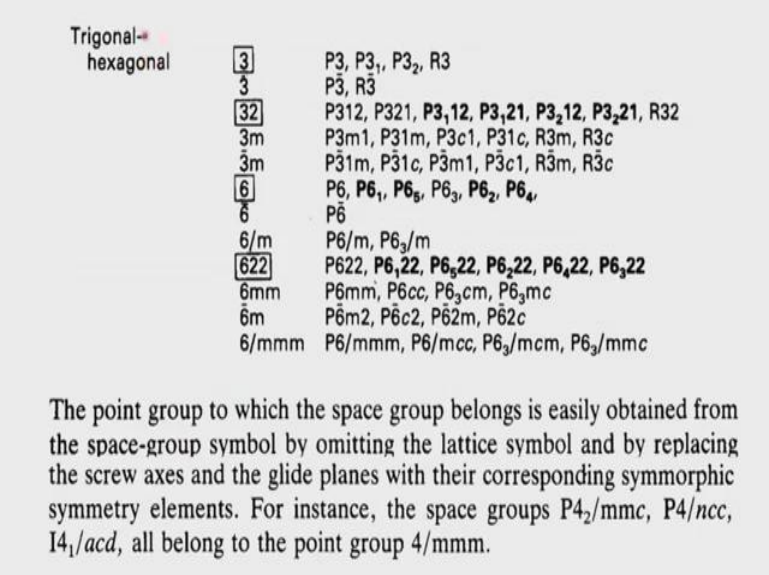


So, what we therefore, see here is the tetragonal the cubic and then of course, trigonal and hexagonal are given here. In case of trigonal and hexagonal again we should have only the primitive lattice in both these cases because you have the angle 120$^o$ in that case $\gamma$ is 120$^o$.

So, we will not have any other body centered and so on and at the same time we also have this rhombohedral symmetry we have not discussed much of rhombohedral symmetry very rarely we come across rhombohedral symmetry compounds; even though they become they are becoming more and more interesting with the fact that some of the perovskite related conductivity conducting materials and so, on have a rhombohedral structure, but that is something which probably is a little advanced for us. So, this from here on we will see how the presence or absence of center of symmetry brings in different natures in the space groups.