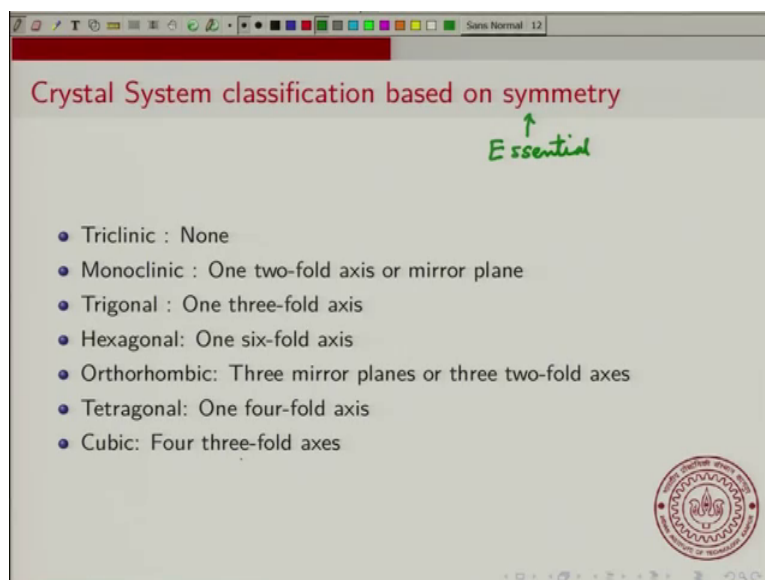


Solid State Chemistry
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Lecture – 22
Crystal Systems and Unit Cells

Now, we will go to the second lecture of week 5 of this course and in this lecture I will continue the discussion on Crystal Systems and Unit Cells. So, week 5 lecture 22 will be Crystal Systems and Unit Cells ok.

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So, in the last lecture we saw the Crystal System classification that was based on symmetry and again we emphasize that this is what we call the essential symmetry and we said that the Triclinic system there is no essential symmetry and we had different systems a Monoclinic has a had one two-fold axis or mirror plane a Trigonal had one three-fold axis, hexagonal the one six-fold axis, Orthorhombic had either 3 mirror planes or three two-fold axis, tetragonal had one four-fold axis and cubic had four three-fold axis ok.

So, these were the essential symmetries for various systems and now what we will see is we will we will look at these symmetries in the context of what we have seen before, which is the shapes of the unit cells. And what we want to see is that we want to look at the unit cell of the crystal and its shape in terms of these symmetries ok.

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Unit Cells

Cubic system \Rightarrow Unit cell satisfies $a=b=c$; $\alpha=\beta=\gamma=90^\circ$

- Shapes of Unit Cells
- Use of parameters $a, b, c, \alpha, \beta, \gamma$
- Restrictions on parameters for different unit cells
- Reduction in symmetry due to unsymmetrical motif

Not a 3-fold axis anymore

Primitive cubic Lattice

NOT A CUBIC SYSTEM

Related to BL

Now, just to remind us so we said that each unit cell has a shape and the general shape is represented as a parallelepiped and this parallelepiped is made of 3 different 3 different abc 3 different vectors which have 3 different angles and show this b slightly differently bc and you can make a parallelepiped using these three segments and you can generate the unit itself.

So, we so we said that you know we showed that you know this is a very convenient way to look at unit cells in terms of abc and there are different angles that we defined. So, the angle between b and c so all this b and c we call it as α between a and b ok. So, this between a and b we called it as γ and between a and c we called it as β ok. So, we have these 3 angles α β γ and these three cell parameters abc ; abc a 3 lens ok.

So, so these 3 lens and 3 angles can be used to specify the shape of the unit cell ok. Now what we said is that for different crystal systems you have different unit cells and these unit cells are specified by a restrictions on the parameters and again what is important is that is that these are unit cells of crystals and these just contain these parameters abc α β γ . So, it just tells you in some sense it tells you what are these parameters of this repeating unit.

Now what we earlier saw is that is that your crystal is a lattice plus basis and we also saw that these unit cells they also they also can be related to Bravias lattices. For example, we

know that some cells some like a like a some unit cells can have primitive face centered body centered or edge centered and so on ok. So, they are related to Bravias lattice and we also saw that the overall crystal is consists of a Bravias lattice and a basis or a motive and this if you have an unsymmetrical motive then there can be a reduction in symmetry ok.

So, the symmetry can be reduced because of presence of an unsymmetrical motive ok. So, for example, if you have a cubic unit cell you have a unit cell that is cubic that is shape like a cube. So, in other words $a = b = c$ $\alpha = \beta = \gamma$ ok.

Now suppose I put some unsymmetrical unit ok, so let me put something that looks like this object and let me take a just a Primitive cubic. So, the lattice is definitely a primitive cubic lattice, but I have this unsymmetrical node.

So, I can write this as primitive cubic lattice plus this motive unsymmetrical motive ok. Now you can see that this threefold axis is not there, so we can see that because of this unsymmetrical motive you rotated 120 degrees, then you can clearly see that these 2 will not go on top of each other ok.

So, the three fold axis is not so this is not a three-fold axis anymore ok. So, even though the unit cell is cubic looks like a cube ok, because of this unsymmetrical motive the it is not a cubic system ok. So, this is not a cubic system. So, it does not belong to a cubic system and this is very important that the symmetry of the crystal is very different from the symmetry of the unit cell.

So, the unit cell is a simple cube ok, but the symmetry of the crystal is very different from that of the unit cell and so given this we think now. However, you can you can also think that suppose you had a cubic system; suppose you had a cubic system and then the unit cell would definitely satisfy $a = b = c$ and $\alpha = \beta = \gamma = 90$ degrees ok.

So, cubic system automatically implies $a = b = c$ $\alpha = \beta = \gamma = 90$ degrees, but not the other way around ok. So, let me write it this way so cubic system implies that must mean that unit cell satisfies $a = b = c$ and $\alpha = \beta = \gamma = 90$ degrees.

However this is not sufficient however, just because a unit cell satisfies this just because a unit cell satisfies $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$, this does not imply a cubic system ok. So, so you could have the same unit cell shape, but a very different system all right ok, so that is to be kept in mind.

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Restrictions on Unit Cells

\neq means NEED NOT BE equal to

- Triclinic : $a \neq b \neq c$; $\alpha \neq \beta \neq \gamma$: None
- Monoclinic : $a \neq b \neq c$; $\alpha = \gamma = 90^\circ$; $\beta \neq 90^\circ$: One 2 or m
- Trigonal(a) : $a = b \neq c$; $\alpha = \beta = 90^\circ$; $\gamma = 120^\circ$: One 3
- Trigonal(b) : $a = b = c$; $\alpha = \beta = \gamma \neq 90^\circ$: One 3
- Hexagonal : $a = b \neq c$; $\alpha = \beta = 90^\circ$; $\gamma = 120^\circ$: One 6
- Orthorhombic : $a \neq b \neq c$; $\alpha = \beta = \gamma = 90^\circ$: Thru 2 or m
- Tetragonal : $a = b \neq c$; $\alpha = \beta = \gamma = 90^\circ$: One 4
- Cubic : $a = b = c$; $\alpha = \beta = \gamma = 90^\circ$: Four 3

Now, now let us look back at these at these restrictions and again what is very important is that you look at these as Restrictions ok. So, Restrictions and what is important while you write these restrictions is to keep in mind that the phrase not equal to means NEED NOT BE equal to be equal to ok.

So, so it need not be it can be equal, but it need not be equal ok. So, so as we said in the triclinic system there is no restriction on abc ok. So, it is often written as a is not equal to b not equal to c, but actually what it means is it is need not be equal to c b it need not be equal to c and alpha need not be equal to beta, need not be equal to gamma ok.

So, so keep in mind that it is not that abc have to be different they could be the same and still it could be Triclinic they could be the same and it could still be triclinic ok. But to be a Triclinic system they need not be equal and the if they are equal it is fine they you can still be a triclinic system even with abc being the same ok, what is what is important is the symmetry of the system.

So, for triclinic what is important is that they should they should satisfy this essential symmetry of 4 of and the essential symmetry is basically none no essential symmetry for a monoclinic. So, for a monoclinic now again a need not be equal to b it need not be equal to c ok, however you should have alpha equal to equal to gamma equal to 90 degrees ok.

So, so actually the restriction is only this is the restriction this is the only restriction and what we will say is that beta need not be 90 degrees, so beta need not be 90 degrees ok. So, the only restriction is that alpha should be equal to gamma equal to 90 degrees.

Now, what is the essential symmetry of a Monoclinic ok. So, it should have 1 2fold axis or mirror plane 1 2 or mirror plane ok. So, so it if has 1 2 or a mirror plane then it is it can be a monoclinic it can be a monoclinic system ok, again it could have more and it would be some other system also.

But if it has 1 2 or m it can be a monoclinic system ok, so that is essential without this you cannot have a monoclinic system without a 2 or an or a mirror you cannot have a monoclinic system ok. Now the Trigonal there are 2 Trigonal there is Trigonal a where the in which case you have a equal to b and it need not be equal to c and you have alpha equal to beta equal to 90 degrees and gamma equal to 120 degrees ok.

So, so this is the this is like one to one third of a hexagonal cell and this the symmetry is the essential symmetry is one 3 axis. So, it should have a if it has a 3 axis then it then you can call it a Trigonal system now Trigonal b is also in the same class. So, that will also have only one 3 axis and again let me circle the restriction. So, the restriction says that a has to be equal to b and alpha has to be equal to beta equal to 90 degrees ok.

So, clearly in a cubic system a is equal to b and alpha equal to beta equal to 90 degrees ok. So, a cubic system can also be a Trigonal system ok. So, that is the that is to be kept in mind now the Trigonal b is in terms of unit cells it is slightly different and this is the r centered r centered Trigonal system.

Here you have a has to be equal to b and it has to be equal to c and alpha beta gamma are equal to each other equal to gamma and they need not be 90 degrees ok. So, they need not be 90 degrees and this also has only one three-fold axis. So, the restriction on the unit cell parameters is that abc are should be the same alpha beta gamma should be the same

that is a restriction on the unit cell parameters and the essential symmetry is that it should have one three-fold axis ok.

What about the Hexagonal? Hexagonal in the hexagonal system again you have you have exactly the same unit cell shape as the as a Trigonal a. So, $a = b$ and need not be equal to c and $\alpha = \beta = 90^\circ$ and oh I should I should emphasize that this is also a restriction and $\gamma = 120^\circ$ that is also a restriction ok.

So, the all these are restrictions, but the essential symmetry for a hexagonal system is 6 fold axis, so it should have a six-fold axis ok. Now for the Orthorhombic system the orthorhombic system we said a is not equal a need not be equal to b it need not be equal to c , however your α has to be equal to β has to be equal to $\gamma = 90^\circ$ ok. So, the restriction is that $\alpha = \beta = \gamma = 90^\circ$ and this has an essential symmetry ok. So, because $\alpha = \beta = \gamma = 90^\circ$ the essential symmetry here is 3. So, it should have not 1 but it should have 3 2 axis or m ok, so three two-fold axis or 3 mirror planes ok.

So, if a system has if a crystal has three two-fold axis or 3 mirrors then it falls in the orthorhombic crystal system it can be an orthorhombic crystal ok. Notice that notice that Monoclinic the essential requirement is 2 or a m ok. So, an orthorhombic system can also be monoclinic ok, it can be monoclinic and but this is the essential symmetry to be orthorhombic and then what about a Tetragonal system? Tetragonal system we said that $a = b$ and it need not be equal to c and $\alpha = \beta = \gamma = 90^\circ$.

Again the essential requirement of tetragonal is that all the 3 angle should be 90° . Now in this case you will have you will have 4 fold axis ok. So, you will have one four-fold axis and finally for a cubic system we have $a = b = c$ $\alpha = \beta = \gamma = 90^\circ$.

So, this is a restriction on the shape of the unit cell ok. So, a cubic system should have this shape of the unit cell and again let me emphasize it just because you have the shape it need not be cubic it can be many other things and it should have 4 three-fold axis that is the essential symmetry ok. So, this is a way to understand how the restrictions on the on the unit cell shape arise for different systems ok.

Now again what is important is that these are only the restrictions are important ok, the not equal to a sin that you see in all these relations ok. That means, it need not be equal to it can be or it may not be ok, but what you know is that for a cubic system.

The unit cell has to satisfy $a = b = c$ $\alpha = \beta = \gamma = 90$ degrees, but it is not I mean it does not imply that every say every unit cell that has $a = b = c$ and $\alpha = \beta = \gamma = 90$ degrees is a corresponds to a cubic crystal ok. So, I will conclude this lecture here and we will now look more closely at the different point groups and space groups in the in the next class.

Thank you.