Symmetry and Structure in the Solid State
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Lecture – 03
Pure Rotation Axes

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So, what we will do next is to see the presence of a 3-fold axes. We saw it already with a different diagram of course there we have different objects, but in this particular case we have a 3-fold axes. Now, the 3-fold axes is illustrated with respect to the presence of a 2-fold two dimensional motif having a 3-fold axes. Now, here I want you to carefully observed this, and identify the nature of the 3-fold axes. There are again in just like in the 2-fold axes situation, we have to put the objects in such a way in this particular motif that they are related by 3-fold symmetry.

So, if they are related by 3-fold symmetry, and there we still demand the close packing, then we have the in this particular case three types of objects. The one in red, the one in white, and the one in black, so three objects. And now I am marking the 0 0 of the 3-fold axes at this position, and I will call it as the origin. So, you see that that the origin there is a 3-fold intersection of this, go back yourself and go to that previous diagram, which I think I will show you again.

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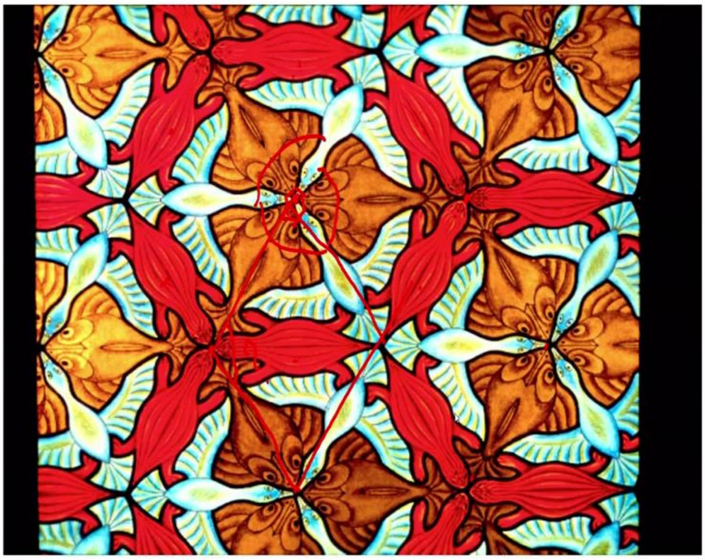

We had this picture, we saw that there is a 3-fold axes which now relates these three objects the three fish. We also have the relation of the three birds, we also found an additional factor that is the presence of the 6-fold arrangement of the tortoise, but then the tortoise are arranged again in with respect to this 3-fold.

So, I have taken this example, which is a much simpler example to illustrate the same. You see that they are identical objects here, they are not different kinds of objects except that the colors are coded differently showing that the orientations are different let us say. So, as a consequence you see that the presence of these three fellows with their tails intersecting at the 3-fold, and the presence of these three white ones inked with the nose intersecting, they generate a 3-fold. And if you now look at the black positions 1, 2, 3 4, 5, 6, they are 6-fold related. And the 3-fold relation we observed with respect to the three black ones here. So, there are two types of possible 3-fold rotations, which can generate this motif.

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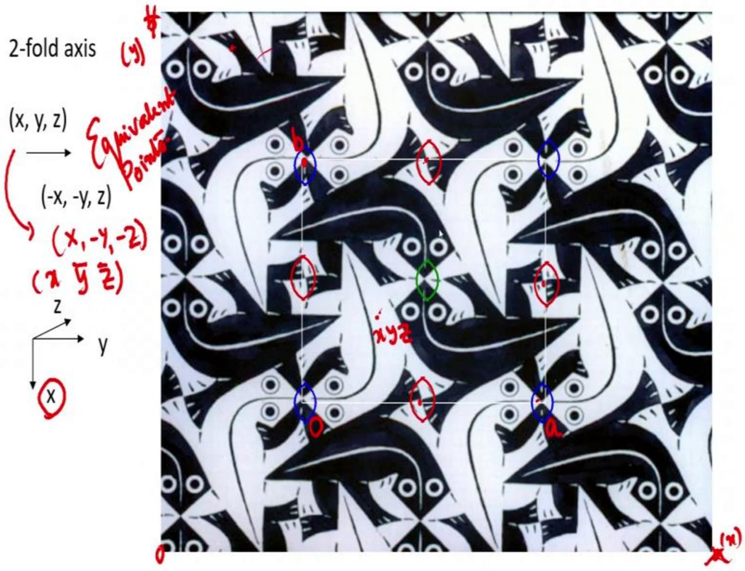

And therefore, it is not just the 3-fold rotation at the positions where we have this is different from the previous case, where we had this results. Here again you see that the job of the 2-fold rotation is the same to rotate the object by 180 degrees, but the object orientation decides how the objects themselves orient.

For example, in this case the noses were related by 2-fold, in this case the legs were rotated by 2-fold, and here the elbow joints were related by 2-fold. And similarly, in this particular case you see that the relationship with respect to the black representation of the object is a 3-fold representation here, and a 6-fold representation here. So, remember the 3-fold and the 6-fold go together. And infact this is something which will observe even in three dimensions.

And therefore, we will get very special cases of the nature of the unit cell when we go to systems, which we are going to define later called a trigonal system, and the hexagonal system. And these this is the kind of origin to the existence of them together in a given unit cell.

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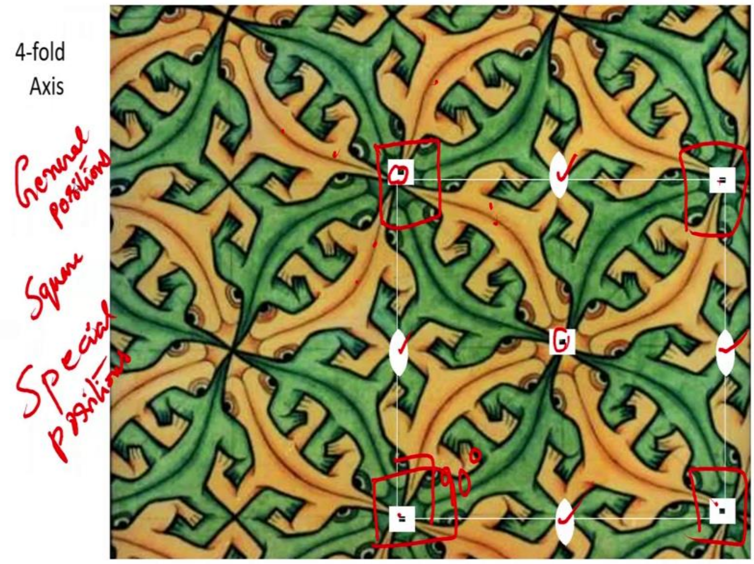

So, you see with two dimensions what we have tried to do so far is to understand the concept of 2-fold, the concept of 3-fold, we can also introduced the concept of 4-fold. Just like the 3-fold and the 6-fold existed together, we also have the 4-fold and the 2-fold existing together in this diagram. This is again a different kind of results different sets of results, we have shown here. And you see that the tales of these three fellows intersect at that point, the tale of this tale of that tale of this, there are four of them now. The angle between them is 90 degrees.

And so this particular unit cell, which I have marked is a unit cell which is a square. Earlier the 2-fold unit cell was at rectangle, that 3-fold unit cell was whatever we had before that is representing the three it was a trigonal unit cell of course we are talking about two dimensions.

So, in two dimensions it has a 3-fold symmetry, it has a 6-fold symmetry. So, 3-fold symmetry, 6-fold symmetry, 4-fold symmetry, and 2-fold symmetry also decides what should be the nature of the lattice, what should be the nature of the unit cell. So that means if a is equal to b and angle is 90 degrees, then you have what is called as a square lattice. So, the square lattice now can be unique in the sense that we have the 4-fold symmetry one once we have this symmetry represent here, we will get the presence of the 4-fold symmetry here as well. But, apart from that we will now generate the 2-fold symmetries at these points, just like we had 3 and 6 there, we have 4 and 2 here.

So, the presence of the 2-fold is inherent in a square lattice, but the 4-fold now dominates by occupying the unit cell edges. Now, these are take home points at this particular point, we are not making any statements the final statements, because we are studying number one the objects in two-dimensions. We are looking only at projections.

And the second one is we are now looking at some abstract objects, we are going to replace these with molecules later on. And look at the molecular symmetry, how the molecular symmetry and the crystal symmetry at simulate together. Just to make life easier at this particular moment, we see that this fellow this lizard has no symmetry. And even though the lizard that does not have any symmetry, the way in which it gets arranged in this lattice produces this 90 degree angles. So, we have this 90 degree angle because of the presence of the lattice.

And therefore, these objects which have no symmetry by themselves can use this 4-fold symmetry, and arrange it themselves in this. There are some time ago there was lot of work done, and imaginations floored you know people imagined various things of how to arrange objects into different kinds of unit cells and so on.

And there was the person by name Kitaigorodsky who found that if the object itself as a certain symmetry, the object itself has a certain symmetry. Suppose, this object has a 4-fold symmetry suppose, it instead of the lizard we have a cubic block ok. And then we now look at the projection down the given axes, let us say it is projected down the cube axes. Then he says he is he found out that if you examine a large number of such objects if the molecule by itself has a symmetry, the molecular symmetry will be utilized by the crystal symmetry.

So, when it goes into the crystalline lattice, you need to goes into this unit cell, the unit cell will now ensure the presence of the molecular symmetry that means, we now not have four of these, but we our cube as mount to sit here at this point. We have also made a remark that each and every point in this particular case will have the cube. So, this will also have the cube, this will also have the cube, this will also have the cube, so that means the molecule now becomes special, we call these are special positions.

And we will be going into the more details one once we understand this symmetry fully, we understand the basics of symmetry, and then we understand how translational periodicity and symmetric can be combined, and how the various crystal systems can be generated. And therefore, we will put all those restrictions together and talk about the general positions and special positions, when we derive the space groups in a much later class.

So, at this particular moment we see that if the molecule as a symmetry Kitaigorodskys finding is that if the molecule has a symmetry, the same symmetry should be maintained in the lattice as well. So, this particular two-dimensional lattice should have that symmetry if the molecule has that symmetry in which case the packing becomes compact, then only we will have the close packing of these objects in such situations.

On the other hand if the object is not having the 4-fold symmetry also or any kind of symmetry as in this example, where there is a lizard sitting here. If they are arranged in such a way that there is a 4-fold symmetry, then the 4-fold lattice can be fitted on to this particular system. So, the objects now are a sitting what we call as general positions.

So, just to tell you about this a little more detail, we now have to derive the so called equivalent points. So, in the 2-fold rotation, we got x, y, z, and x bar, y, z bar. And then we have to now look at what happens, when we have a 4-fold symmetry, what happens when we have a 2-fold symmetry and so on. So, this is the next step to which we go, and this step which we take up to do that will come a little later, because I want to introduce you to the opposite congruence objects.

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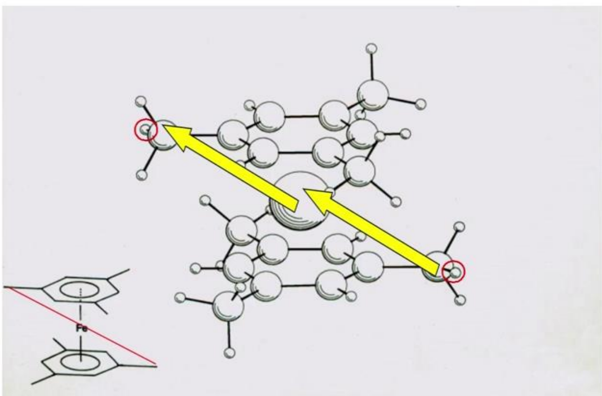

Centre of symmetry (x, y, z) ⟶ (-x, -y, -z)

So, we so far we have looked at only the direct congruence objects. So, the objects of opposite congruence, and I am giving you an example from literature and that of a molecule. In this particular case, I have shown the molecule ferrocene and not ferrocene, this is a diphenyl iron is not ferrocene. Ferrocene will have a five membered ring system, this as a six membered ring. So, we have the diphenyl, and iron is at the centre.

Now, the way the molecule appears the molecular symmetry appears is the presence of given any x, y, z, it can go to -x -y -z. So, this is an inversion symmetry, centre of symmetry, we call this has the centre of symmetry being present at this particular position. So, the molecule is centre of symmetry. So, by the logic which we use now so far in case of direct congruence objects; if the molecular is central symmetric, then the molecule has to go into a crystal system which is also a center of symmetric.

So, the lattice we chooses should also have a center of symmetry, not just that the lattice is chooses should have its center of symmetry coincident with the center of symmetry in the molecule. So, the molecule has a certain symmetry, and there is no further freedom given to the molecule, the molecule still sits in a position with which it will generate the center of symmetry.

So, the molecule symmetry, and the lattice symmetry will have to have a center of symmetry, because this space in which this molecule is now going to be put either it is two-dimensional or three-dimensional will have x, y, z to -x -y -z every point in this space will be going from x, y, z to -x -y -z. So, the molecular symmetry, therefore dominates this is how Kitaigorodsky observed it. So, I thought I will give an example with a object of indirect congruence.

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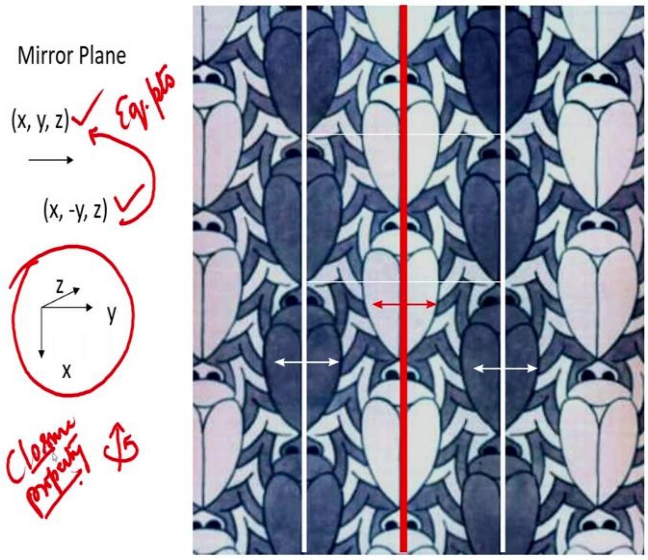

Object of opposite or indirect congruence can also have mirror planes, this is an example where Escher's diagram again I have used, in order to illustrate the presence of a mirror plane. You see we talked about points centre of symmetry, we talked about axes of rotation about which the rotation takes place 2, 3, 4 and 6; 1, 2, 3, 4 and 6 or the axes of rotation. We have the point of symmetry which is the centre of symmetry.

In this particular case, we had this molecule just now discuss the iron compound, where iron is sitting at the centre of symmetry. So, we have the rotation axis and points as we said in the very first class that we have symmetry elements, which can be points, which can be axes, which can also be planes. So, this particular plane is a plane which is now defining the x, y, z if we define in this particular mirror in which we have shown here, the coordinate system you see that the there is a change in the y axis, in the y direction, so x, y, z has gone to x, minus y, z.

So, what happens in this particular case is that there is a plane, which passes through the centre of this beetles, and you see that the right hand side of the beetles is identical to the left hand side of the beetles, and this goes through the entire motif. So, we define what we call as a mirror plane. So, this mirror plane is now, in the plane of this is the y direction. So, the mirror plane is coming in such a way that we also invoke the presence of mirror planes with the other object, which is now the black object the black beetles that also is related by a mirror plane this also is related by mirror planes. So, the mirror plane propagates through the entire lattice generating a close packed motive.

So, in this particular case what is required is in case of the centre of symmetry, we needed a point. Here we in the case of the rotation axes, we need an axes of rotation about which the rotation occurs, it could be a 2-fold, 3-fold, 4-fold, 6-fold, whereas in this particular case mirror stands out by itself. So, in this case the mirror is perpendicular, and we call it a mirror plane which is perpendicular to the in this particular case the x, z plane. So, mirror is cutting through this. So, we have this side is mirror image of that side.

So, it is like I put my left hand here, and my right hand here, and this now are related through this mirror plane. So, you see that the overlap of the objects will occur that way only if we now take this image, and take the image which is the left hand. So, with the right and left hand define what are known as and enantiomorphous objects. So, the object in fact, these two are not going to be identical otherwise. See nobody is left hand is identical to anybody is right hand, then it will be a terrible issue is it matter. If both of them are identical and thereby real space, they are related to each other, then our hands will be in a different I do not know what orientation I have to show you, but it would not be like that.

So, it has to therefore have the two objects, therefore my left hand and the right hand or enantiomorphous objects. So, the symmetry that is associated with a mirror is an enantiomorphic. What do you think is the symmetry that is associated with the centre of symmetry? This should also now be an object, where the right hand side this side of the object is now going to -x, -y, -z. So, when we there is a change of value of x, y, and z, all three changing from x, y, z then also I have an inversion.

So, the inversion is also an operation, where the object can be also not necessarily, and in fact it is not a enantiomorphous objects. So, enantiomorphous objects are very special, and therefore the enantiomorphous behaviour in the arrangement of molecules will also be different. And this happens in case of many of these amino acids particularly the naturally occurring amino acids. The naturally occurring amino acids are have a rotation, the optical rotation, there have the levo or dextro rotatory, and most of the naturally occurring amino acids are levorotatory.

And therefore, when you arrange these molecules into a protein the structure of the protein always can never go into a centre of symmetric system, it has to go into a non-centre of symmetric system, because it has to have the so called enantiomers behavior. So, the objects that compound a protein will be enantiomorphous object, and is something which is very interesting in biology and in fact the most of biology is a matter of fact consequence of the presence of a enantiomeric objects in protein structures. That important point is something which will cleans the whole issue that is suppose you have let us go back to the centre of symmetry or for that matter we can go to this mirror.

So, in the case of the mirror operation, we take x, y, z to x -y z. So, the point from here went to the other point. Now, suppose I operate a mirror plane again on this fellow x, y bar, z, what will happen x, y bar z will go back to expression. So, x, y, z and x, y bar, z are the two equivalent points or the two equivalent points, which are related by this symmetry operation, we call this as the symmetry operation the related by the symmetry operation. These are the two equivalent points. And no other equivalent point exist in this diagram for this time that means, x, y, z goes to x, y bar, z and x, y bar, z goes back to x, y, z.

So, the whole this thing the closing, it is referred to as a closure property. And in this brings in the issue of group theory, so in group theory we call such operations has operations of a group. Now, there are various ways in which we can approach this problem, we can go into a conventional group theoretical way of doing things, but then I thought that it is not the way we will go about. Instead, we will keep this in mind that when we have these equivalent points, operation of the equivalent point once again will take it back to the original, depending on what kind of situation we are in, if there is only one mirror plane operation, x, y, z goes to x, y bar z, and x, ybar z goes back to x, y, z.

Now, this kind of a thing will therefore close the whole issue that means, we cannot have any more objects. If I have an object here, object here, these two objects only are there in this particular unit cell, beyond that we cannot have any more objects. The next unit cell is only a translational periodicity repeated thing, and therefore this will now repeat itself in the next unit cell, it will repeat in the both directions a and b.

And therefore, the existence of points x, y, z, and x, y bar, z they define such a situation in mathematics is referred to as a group. So, they define a closure property, and therefore this defines a group property. So, the points now belong to a group. There is a clear cut mathematical procedure through which we can understand, what is group, there is a group theoretical principle. And we can design now the so called methodology for using this group theoretical information to identify what are known as point groups, and space groups.

In fact, the presence of point groups and space groups, we will bring it in a totally different contacts. And then relate what we have seen in these diagrams once again to whatever we have achieved so far, so that you know you get a one to one correspondence, without going into the rigor of mathematics, which is involved in group theoretical methodology. Even though that is probably not the method to follow the group theoretical behaviour.

In this particular case, particularly for chemist and biologist which will be very useful to understand what we are doing in terms of these pictures. And also now eventually when we do the point groups and space group, how we derive this point groups and space groups or rather than how mathematics arrives at that, because the mathematically deriving thing is straight forward, and very easy from the mathematics point of view. But, from the understanding point of view, the way we are going to do in terms of group theory, and the particularly the point group derivation and space group derivation will be a better way of understanding. The three dimensional architecture in molecular crystals crystalline materials, which are molecules or ions or whatever it is easier to get a picture of that .

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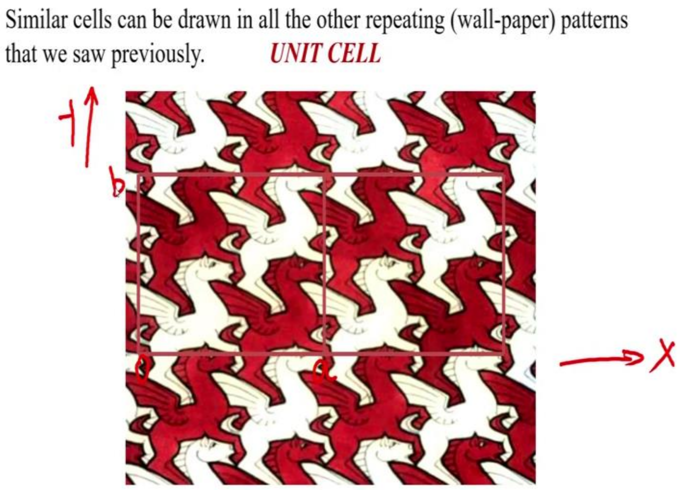

So, we saw the glide plane. So, what is important here is something which we defined already we have been talking about it, but we have not put it in a real nutshell. So, what you know it is like as I always tell in my regular class, what we have done today in the last few classes, I think it is now the class number-3 as far as time is concerned.

So, in the last three classes is to get the alphabets is it something like developing a grammar, we are now trying to developed the grammar of crystallography, and the grammar of symmetry and structure particularly. So, to develop the grammar, we are now looking at various alphabets. So, what we have got so far is in terms of the definitions of close packing, the presence of symmetry. The presence of symmetry in two dimension, and eventually we will extend to three dimensions. And we have use the two dimensional drawings of (Refer Time: 23:05) to get a feel for what are the types of symmetry elements, they that can be there to describe the two dimensional motives which are already displayed.

So, in this particular context, we have been talking about the definition of what we have been referring to as the unit cell. The unit cell is something which repeats itself in both the directions, in this case it is two dimensional. So, you this marking which I have done in red will define the so called unit cell that means, whatever is there inside, which is now atoms and molecules and so on, instead of these objects. Whatever is there inside this box will repeat exactly the same way in the next box, it does not mean that I have to fix the origin here, I can fix the origin wherever you want. So, it is like you know the window frame. If you want to fix window frame, and in a building all the windows are identical, the size the dimensions of the windows are identical. So, we have to now generate frames.

Now, the frames which we generate or the unit cells. So, we can take the unit cell fix it to this window on the right, window on the left, window in the back, window in the front, because as far as the dimensions are concerned they remain the same. So, similarly unit cells therefore can be defined in such a way that they are like frames.

So, we can move this along anywhere in the two dimensional space, it will fit exactly the symmetry that is required for this two dimensional motif, so that way we define the unit cell here. In terms of let now I can call this as 0, the 0 are the origin can be anywhere in this diagram. So, we have decided to fix it there, then this distance will be a zero to a along the x axis x direction, and in the y direction we see that this is b.

Now, if we go back to the 3-fold case here, you see suppose I call this as 0 and this angle is very crucial now. So, if these are the vector, so this vector is now a, and this vector is now b ok. So, effectively what happens is this now defines the unit cell 0 b, and 0 a. You see that this is not if we take this as on the x axis, if the 0 a along the x axis, b need not be along the x axis. So, the presence of the b will be in such a way that we have to now define the direction of b, it is not with respect to the 90 degree angle. And so this becomes an issue in case of 3-fold and 6-fold, it is not an issue in case of the 2-fold and the 4-fold ok, so remember this, we will see why it is so important later.

So, in this particular example coming back to the definition of a unit cells. So, we define this unit cell as a repeat unit, it repeats itself in two dimensions to describe our entire motif. So, the unit cell is drawn in all other repeating wall pattern patterns, so just to show that the unit cells can be drawn for all the diagrams, we have shown in the (Refer Time: 26:37).

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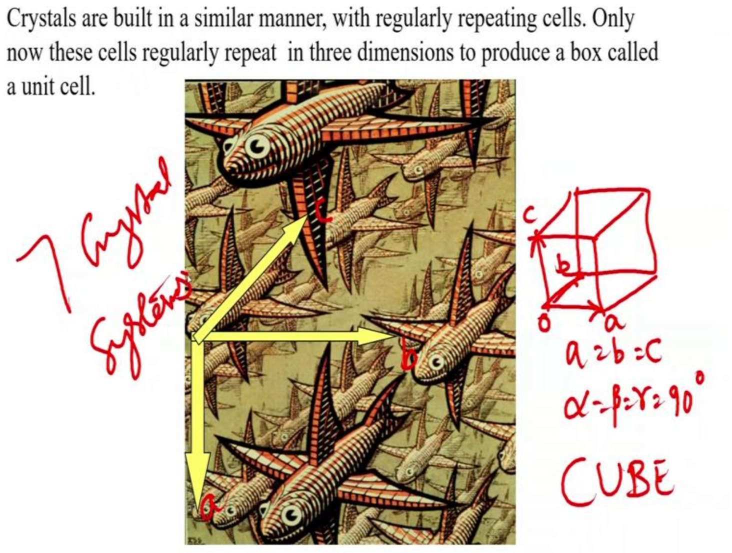

Now, coming to the last part of today’s this particular class, we will see that the two dimensions can be extended to three dimensions, because now we are in a situation to go towards three dimensions. So, just like we have the concepts built in two dimensions, the extend this to two three dimensions.

And we therefore have the direction a, direction b, and direction c. Remember a, b, and c need not always be rectilinear coordinates, they need not be rectangles of 90 degrees depends upon the symmetry. If this symmetry allows for a, b, c to be at 90 degrees with respect to each other, then only then and then only we can have the unit cell definition ok, this is very important to remember at this moment.

So, this produces now a box. So, the box can be it like this with all 90 degree angles. And if a is equal to b is equal to c alpha, beta, gamma the angle between these a, b, and c or 90 degrees, then we call this a cube. So, this will be one of the possible unit cells, which can we can have in a three dimensional description of the crystal structure. So, with crystals can grow into cubic cells.

We will see how many possible cells are going to come in the next class, and in what way they appear. And the consequences of how the angles play a very important role, and the concept of vectors that means, we are now it depends upon where the origin is define the concept of vector a, vector b, and vector c the way in which we define a, b, and c. And the angle interracial angle between them becomes crucial to define the crystal geometry.

And the three dimensional unit cells, which will develop cannot be all kinds of unit cells, because it has to have the information about the symmetry we have understood. So, combination of symmetry, and the requirement of the three dimensionality in the unit cell, which preserves the symmetry it will allow only certain set of possible unit cells. And that is how we end up with seven crystal systems ok. So, today’s class will end at this particular moment, and we will go further.

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C. Giacavazzo (Ed.) Fundamentals of crystallography,
J. D. Dunitz, X-ray analysis and the structure of organic molecules
G.H. Stout and L.H. Jensen

Now, before I go further, I just thought I should give you three reference books. One is the book of fundamentals in crystallography, it is an IOCR text, and this is by Carmelo Giacavazzo. And some of the contents of today’s talk is taken from there. The (Refer Time: 29:25) diagram, and the way in which it develops and so on is my own imagination. And so it is dependent upon how you view it, and how one use views it. So, I thought that that will be the best approach to give you the concept clear.

And then the next class, we will go and try to understand the concepts of how to represent these symmetries, how the symmetries accumulate. And we now then go into the aspect of what we called as point group symmetries. So, the next book is by Jack Dunitz, it is X-ray analysis and structure of organic molecules. This is a book where we you will find some very basic understanding of the X-ray diffraction theory, and then how it refers to the molecular species. The fundamentals of crystallography will cover overall all the aspects.

There is another book by Stout and Jensen. This is a book on X-ray structure analysis practical guide, I did not write it down here, but it is X-ray structure analysis a practical guide. And that book is bit ancient, but at the same time it gives as the required basics. So, what you will see in the coming classes will be that I will be using these concepts in and out, on and off.

So, books of this these books will be referred to once in a while. And whenever I refer to that I will mention I have taken it from this particular books, so that when you have to practice what you want to do in future with this course, then and you are guy got hold of these books, it will help you to find out where we are now referring to at that particular moment ok. So, I think we will stop here for today.

Thank you.