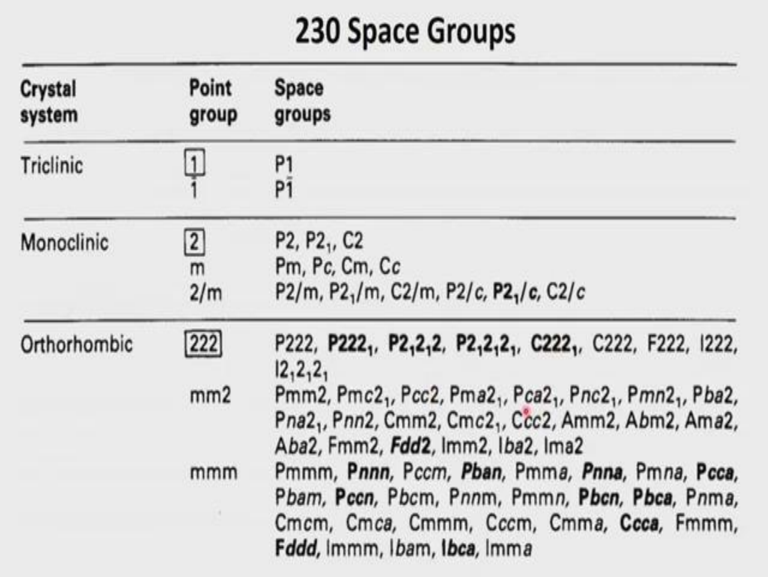
Symmetry and Structure in the Solid State
Prof. T. N. Guru Row
Solid State and Structural Chemistry Unit
Indian Institute of Science, Bangalore

Lecture – 29
Atoms in the Crystal: Positions and Relevant Properties

We have been looking at the total space groups in the form of a table.

(Refer Slide Time: 00:35)



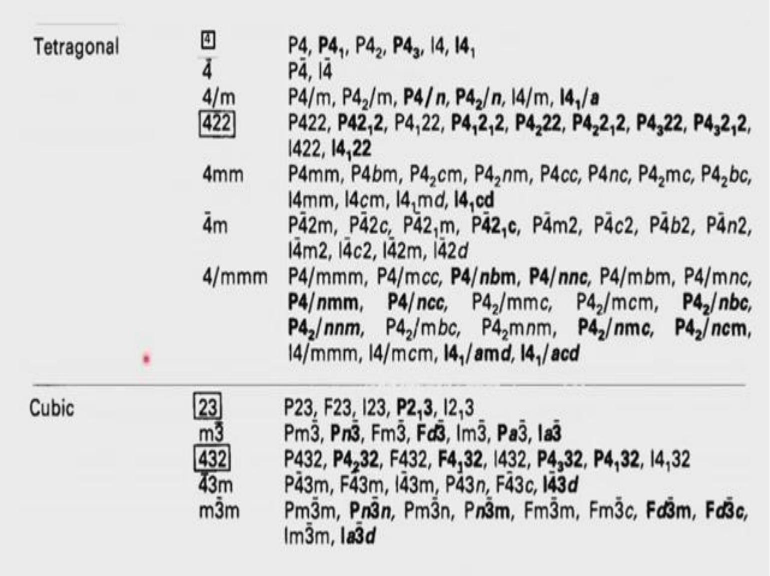
230 Space Groups

Crystal system	Point group	Space groups
Triclinic	$\boxed{1}$	P1
	$\bar{1}$	$P\bar{1}$
Monoclinic	$\boxed{2}$	P2, $P2_1$, C2
	m	Pm, P*c*, Cm, C*c*
	2/m	P2/m, $P2_1/m$, C2/m, P2/*c*, **$P2_1/c$**, C2/*c*
Orthorhombic	$\boxed{222}$	P222, **$P222_1$**, **$P2_12_12$**, **$P2_12_12_1$**, **$C222_1$**, C222, F222, I222, $I2_12_12_1$
	mm2	Pmm2, $Pmc2_1$, P*cc*2, $Pma2_1$, $Pca2_1$, $Pnc2_1$, $Pmn2_1$, P*ba*2, $Pna2_1$, P*nn*2, Cmm2, $Cmc2_1$, C*cc*2, Amm2, A*b*m2, Am*a*2, A*ba*2, Fmm2, ***Fdd*2**, Imm2, I*ba*2, Im*a*2
	mmm	Pmmm, ***Pnnn***, P*ccm*, ***Pban***, Pmm*a*, ***Pnna***, Pm*na*, **P*cca***, P*bam*, **P*ccn***, P*bcm*, P*nnm*, Pmm*n*, **P*bcn***, **P*bca***, P*nma*, Cm*cm*, Cm*ca*, Cmmm, C*ccm*, Cmm*a*, **C*cca***, Fmmm, ***Fddd***, Immm, I*bam*, **I*bca***, Imm*a*

And this particular table is something which is very useful for cross references back and forth reference and so on. As we saw that it tells us about the lattice symmetry as well as the symmetry that can be associated with the space group the point group symmetry. It also tells us about the types of distribution of centric and non centric systems which can come with the triclinic monoclinic orthorhombic and the other crystal systems.

So, we see that in the case of the orthorhombic system all possible lattices are there. So, we generate the *P* lattice, we generate the *C* lattice, we generate the *F*, as well as the *I*.

(Refer Slide Time: 01:17)



Tetragonal	$\boxed{4}$	$P4$, **$P4_1$**, $P4_2$, **$P4_3$**, $I4$, **$I4_1$**
	$\bar{4}$	$P\bar{4}$, $I\bar{4}$
	$4/m$	$P4/m$, $P4_2/m$, **$P4/n$**, **$P4_2/n$**, $I4/m$, **$I4_1/a$**
	$\boxed{422}$	$P422$, **$P42_12$**, $P4_122$, **$P4_12_12$**, **$P4_222$**, **$P4_22_12$**, **$P4_322$**, **$P4_32_12$**, $I422$, **$I4_122$**
	$4mm$	$P4mm$, $P4bm$, $P4_2cm$, $P4_2nm$, $P4cc$, $P4nc$, $P4_2mc$, $P4_2bc$, $I4mm$, $I4cm$, $I4_1md$, **$I4_1cd$**
	$\bar{4}m$	$P\bar{4}2m$, $P\bar{4}2c$, $P\bar{4}2_1m$, **$P\bar{4}2_1c$**, $P\bar{4}m2$, $P\bar{4}c2$, $P\bar{4}b2$, $P\bar{4}n2$, $I\bar{4}m2$, $I\bar{4}c2$, $I\bar{4}2m$, $I\bar{4}2d$
	$4/mmm$	$P4/mmm$, $P4/mcc$, **$P4/nbm$**, **$P4/nnc$**, $P4/mbm$, $P4/mnc$, **$P4/nmm$**, **$P4/ncc$**, $P4_2/mmc$, $P4_2/mcm$, **$P4_2/nbc$**, **$P4_2/nnm$**, $P4_2/mbc$, $P4_2mnm$, **$P4_2/nmc$**, **$P4_2/ncm$**, $I4/mmm$, $I4/mcm$, **$I4_1/amd$**, **$I4_1/acd$**
Cubic	$\boxed{23}$	$P23$, $F23$, $I23$, **$P2_13$**, $I2_13$
	$m\bar{3}$	$Pm\bar{3}$, **$Pn\bar{3}$**, $Fm\bar{3}$, **$Fd\bar{3}$**, $Im\bar{3}$, **$Pa\bar{3}$**, **$Ia\bar{3}$**
	$\boxed{432}$	$P432$, **$P4_232$**, $F432$, **$F4_132$**, $I432$, **$P4_332$**, **$P4_132$**, $I4_132$
	$\bar{4}3m$	$P\bar{4}3m$, $F\bar{4}3m$, $I\bar{4}3m$, $P\bar{4}3n$, $F\bar{4}3c$, **$I\bar{4}3d$**
	$m\bar{3}m$	$Pm\bar{3}m$, **$Pn\bar{3}n$**, $Pm\bar{3}n$, **$Pn\bar{3}m$**, $Fm\bar{3}m$, $Fm\bar{3}c$, **$Fd\bar{3}m$**, **$Fd\bar{3}c$**, $Im\bar{3}m$, **$Ia\bar{3}d$**

Now, all these lattices except the *C* lattice gets generated in the case of a cube. So, we will have the *P* *F* and *I* allowed in the case of a cube the only condition is that the threefold symmetry which is a basic symmetry in a cubic system appears along the 1 1 1 direction.

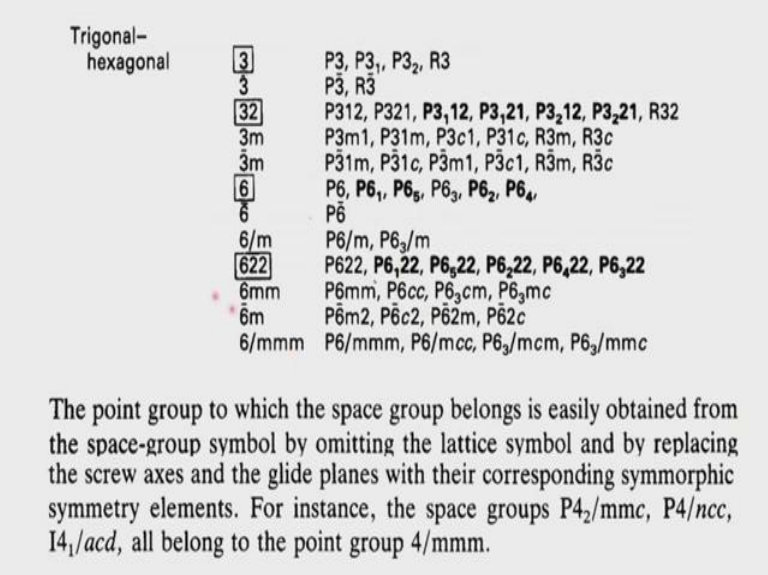
In case of the tetragonal system there is only possibility of primitive as well as the body centered. And we see that $4/m$ is the one in which we will have the center of symmetry getting in. And also in the case of $4/m\ m\ m$ center of symmetries space groups get coming; the rest of the symmetry elements I put a question in the previous discussion that if $\bar{2}$ is mirror then it is non centrosymmetric.

So, if what is $\bar{4}$? So, $\bar{4}$ is also non centrosymmetric and that goes into generating space groups $P\ \bar{4}$ and $I\ \bar{4}$. So, $4/m$ and the $4/m\ m\ m$ are the ones we generate the; so there are large number of possible non centrosymmetric systems in a tetragonal system. And if one looks at the literature and looks at all the magnetic materials; the magnetic materials belong to higher systems particularly the inorganic based magnetic materials; inorganic material based magnetic materials. And many of them are the distorted perovskites and so on; they all go into the tetragonal system and they go into non centrosymmetric tetragonal systems.

So, many of the ferroelectric systems go into tetragonal systems. So, if an organic ferroelectric is crystallizing; you know tetragonal system it will be very excited because such a compound will certainly have a very high hysteresis behavior and so on. So, what I am trying to tell is that the property that comes eventually for the material is already a part and parcel built in due to the symmetry.

So, the symmetry now decides what should be the property in a given particular direction in the crystal. So, that way a crystal is not always isotropic; the property in a crystal therefore, depends upon in which direction we measure or in which plane perpendicular to which we measure and so on the property. It also depends upon how the atoms align themselves or arrange themselves in these space groups as we discussed in case of calcium carbonate and CuO.

(Refer Slide Time: 03:45)



Trigonal–hexagonal	$\boxed{3}$	P3, $P3_1$, $P3_2$, R3
	$\bar{3}$	$P\bar{3}$, $R\bar{3}$
	$\boxed{32}$	P312, P321, $\mathbf{P3_112}$, $\mathbf{P3_121}$, $\mathbf{P3_212}$, $\mathbf{P3_221}$, R32
	3m	P3m1, P31m, P3*c*1, P31*c*, R3m, R3*c*
	$\bar{3}m$	$P\bar{3}1m$, $P\bar{3}1c$, $P\bar{3}m1$, $P\bar{3}c1$, $R\bar{3}m$, $R\bar{3}c$
	$\boxed{6}$	P6, $\mathbf{P6_1}$, $\mathbf{P6_5}$, $P6_3$, $\mathbf{P6_2}$, $\mathbf{P6_4}$,
	$\bar{6}$	$P\bar{6}$
	6/m	P6/m, $P6_3/m$
	$\boxed{622}$	P622, $\mathbf{P6_122}$, $\mathbf{P6_522}$, $\mathbf{P6_222}$, $\mathbf{P6_422}$, $\mathbf{P6_322}$
	6mm	P6mm, P6*cc*, $P6_3cm$, $P6_3mc$
	$\bar{6}m$	$P\bar{6}m2$, $P\bar{6}c2$, $P\bar{6}2m$, $P\bar{6}2c$
	6/mmm	P6/mmm, P6/m*cc*, $P6_3/mcm$, $P6_3/mmc$

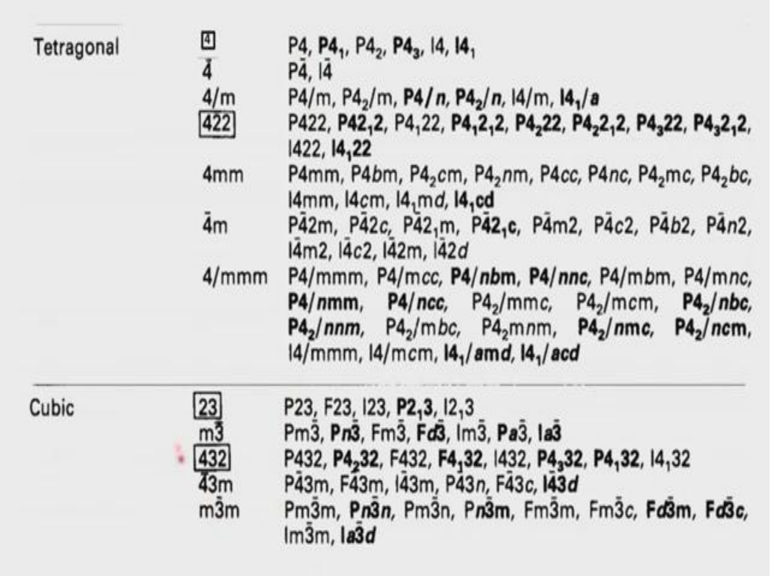
The point group to which the space group belongs is easily obtained from the space-group symbol by omitting the lattice symbol and by replacing the screw axes and the glide planes with their corresponding symmorphic symmetry elements. For instance, the space groups $P4_2/mmc$, $P4/ncc$, $I4_1/acd$, all belong to the point group 4/mmm.

So, therefore, we have reached a stage where we now consolidate the information which we have on all their space groups before we go further.

So, for example, the point group to which the space group belongs is easily obtained from the space group symbol by omitting the lattice symbol and by replacing the screw axis and the glide planes, with their corresponding symmorphous symmetry elements. What it means to say is for example, if you have a space group like $P\ 6_5\ 2\ 2$ you delete the *P*, make 6_5 into 6 and you get the point group 6 2 2. So, that is how we can determine given the space group we can determine the point group.

Given the point group we can predict what are all the possible space groups ok; the number of space group that are possible for a threefold symmetry is 1 2 3 4, if there is only 3 associated with it. In case of $6/m\ 2/m\ 2/m$ we will get so many 4 of them as possible symmetry for space groups.

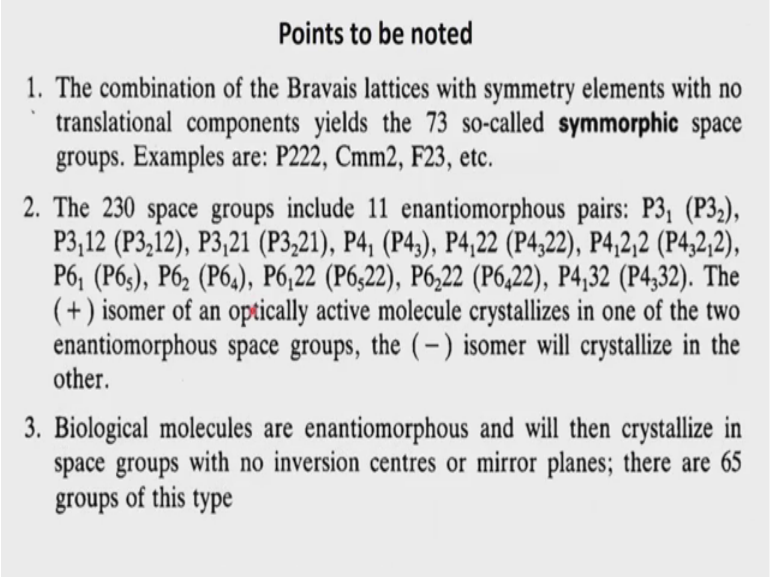
(Refer Slide Time: 04:49)



Tetragonal	$\boxed{4}$	$P4$, **$P4_1$**, $P4_2$, **$P4_3$**, $I4$, **$I4_1$**
	$\bar{4}$	$P\bar{4}$, $I\bar{4}$
	$4/m$	$P4/m$, $P4_2/m$, **$P4/n$**, **$P4_2/n$**, $I4/m$, **$I4_1/a$**
	$\boxed{422}$	$P422$, **$P42_12$**, $P4_122$, **$P4_12_12$**, **$P4_222$**, **$P4_22_12$**, **$P4_322$**, **$P4_32_12$**, $I422$, **$I4_122$**
	$4mm$	$P4mm$, $P4bm$, $P4_2cm$, $P4_2nm$, $P4cc$, $P4nc$, $P4_2mc$, $P4_2bc$, $I4mm$, $I4cm$, $I4_1md$, **$I4_1cd$**
	$\bar{4}m$	$P\bar{4}2m$, $P\bar{4}2c$, $P\bar{4}2_1m$, **$P\bar{4}2_1c$**, $P\bar{4}m2$, $P\bar{4}c2$, $P\bar{4}b2$, $P\bar{4}n2$, $I\bar{4}m2$, $I\bar{4}c2$, $I\bar{4}2m$, $I\bar{4}2d$
	$4/mmm$	$P4/mmm$, $P4/mcc$, **$P4/nbm$**, **$P4/nnc$**, $P4/mbm$, $P4/mnc$, **$P4/nmm$**, **$P4/ncc$**, $P4_2/mmc$, $P4_2/mcm$, **$P4_2/nbc$**, **$P4_2/nnm$**, $P4_2/mbc$, $P4_2mnm$, **$P4_2/nmc$**, **$P4_2/ncm$**, $I4/mmm$, $I4/mcm$, **$I4_1/amd$**, **$I4_1/acd$**
Cubic	$\boxed{23}$	$P23$, $F23$, $I23$, **$P2_13$**, $I2_13$
	$m\bar{3}$	$Pm\bar{3}$, **$Pn\bar{3}$**, $Fm\bar{3}$, **$Fd\bar{3}$**, $Im\bar{3}$, **$Pa\bar{3}$**, **$Ia\bar{3}$**
	$\boxed{432}$	$P432$, **$P4_232$**, $F432$, **$F4_132$**, $I432$, **$P4_332$**, **$P4_132$**, $I4_132$
	$\bar{4}3m$	$P\bar{4}3m$, $F\bar{4}3m$, $I\bar{4}3m$, $P\bar{4}3n$, $F\bar{4}3c$, **$I\bar{4}3d$**
	$m\bar{3}m$	$Pm\bar{3}m$, **$Pn\bar{3}n$**, $Pm\bar{3}n$, **$Pn\bar{3}m$**, $Fm\bar{3}m$, $Fm\bar{3}c$, **$Fd\bar{3}m$**, **$Fd\bar{3}c$**, $Im\bar{3}m$, **$Ia\bar{3}d$**

for instance the space group $P\ 4_2/m\ m\ c$, $P\ 4/n\ n\ c$; so, we have taken the case of the tetragonal system. So, if you take $P\ 4_2/m\ m\ c$ it will be actually $4/m\ 2/m\ 2/m$ which corresponds to $4/m\ m\ m$. So, it is very easy to find out therefore, given the space group the corresponding point group symmetry.

(Refer Slide Time: 05:08)



Points to be noted

1. The combination of the Bravais lattices with symmetry elements with no translational components yields the 73 so-called **symmorphic** space groups. Examples are: P222, Cmm2, F23, etc.
2. The 230 space groups include 11 enantiomorphous pairs: $P3_1$ ($P3_2$), $P3_112$ ($P3_212$), $P3_121$ ($P3_221$), $P4_1$ ($P4_3$), $P4_122$ ($P4_322$), $P4_12_12$ ($P4_32_12$), $P6_1$ ($P6_5$), $P6_2$ ($P6_4$), $P6_122$ ($P6_522$), $P6_222$ ($P6_422$), $P4_132$ ($P4_332$). The (+) isomer of an optically active molecule crystallizes in one of the two enantiomorphous space groups, the (−) isomer will crystallize in the other.
3. Biological molecules are enantiomorphous and will then crystallize in space groups with no inversion centres or mirror planes; there are 65 groups of this type

The other points that have to be noted are the following; see suppose you have a have the Bravais lattices with symmetry elements with no translational components; that means, there is no 2_1 screw axis, no glide planes and so on.

So, if you look at count the number of such space groups we have the space groups now corresponding to the total number of 73. So, out of the 230; 73 are called symmorphic space groups; the examples are *P* 2 2 2, *C m m* 2 *F* 2 3 etc., Notice that the lattice centering is immaterial, what is important is the non translational symmetry operation with respect to the point group operation.

So, the point group operation should not have the point group should not be now accompanied by translational components like the screw axis and the glide planes. But as far as the lattice nature is concerned we can have all the possible lattices. So, if we count all of them out of the 230; we get 73 of them and these are called symmorphic space groups.

Apart from that in the 230 space groups there are some eleven of them which are quite interesting space groups; these are called enantiomorphous its like the right hand and the left hand pairs. For example, if you take $P\ 3_1$; the 3_1 axis in the case of 3_1 is the translations are one third, two third and full to get the $P\ 3_1$ operation. For the $P\ 3_2$ operation it is two third and then it is one third in the next unit cell which can be brought back to the previous unit cell.

So, the handedness if the first one is considered right handed the second one will be left handed. So, that is why they are referred to as an enantiomorphous pairs. So, we have these many space groups which are enantiomorphous pairs and what happens in these case of enantiomorphous pairs is very interesting when we deal with optically active molecules.

So, when optically active molecules crystallize the let us say there are 2 isomers the first isomer which we will call as positive can crystallize in one of the enantiomorphous space group; then the opposite number will crystallize in the other case. We still do not know either to identify the plus with the clockwise rotation or minus with the anti clockwise direction.

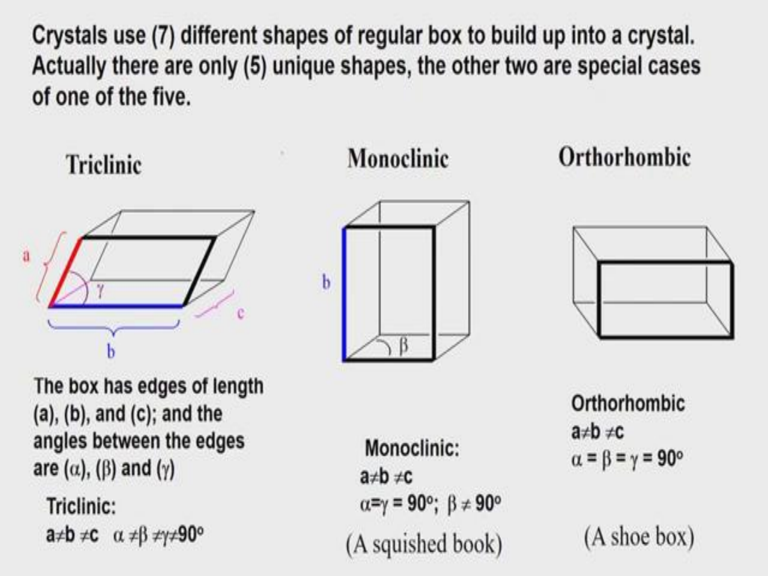
But that is something we will be able to determine by making use of a technique which is very very specially associated with X ray diffraction and that technique is known as anomalous dispersion. I do not know whether we will have time to cover that aspect in this course; it is very advanced methodology, but maybe we will mention it in the passing towards the later part of the class.

So, therefore, it is there possible by X ray diffraction therefore, to determine the absolute configuration. So this is if the plus isomer is in one form and minus isomer in the other form; in principle we are now looking at the absolute configuration of the given material. Whether it is levorotatory or dextrorotatory or whether it is R or S molecule and we can also point out this is R molecule and this is S molecule if we do anomalous dispersion. And that is how it that technique becomes extremely useful; particularly in case of a compounds which can crystallize both in R and S forms, the isolation of R and S by crystallization methodology can be accounted for.

Biological molecules these are also very exciting because there are more and more accumulation of very large molecules. People are now looking at protein protein interactions people are looking at protein steroid interactions and so on. So, these molecules are enantiomorphous; it does not mean that they will go only into these 11 enantiomorphous pairs; they will of course, go into only crystals crystal systems and space groups which have no inversion centers or mirror planes; there are 65 of them.

So, out of it 230 when you do the structures of biological molecules particularly in a naturally occurring native proteins and so on; there are only 65 space groups that are allowed. So, these are points that one has to remember with respect to 230 space groups.

(Refer Slide Time: 09:46)



Crystals use (7) different shapes of regular box to build up into a crystal. Actually there are only (5) unique shapes, the other two are special cases of one of the five.

Triclinic

The box has edges of length (a), (b), and (c); and the angles between the edges are (α), (β) and (γ)

Triclinic:

$a \neq b \neq c \quad \alpha \neq \beta \neq \gamma \neq 90^\circ$

Monoclinic

Monoclinic:

$a \neq b \neq c$

$\alpha = \gamma = 90^\circ; \ \beta \neq 90^\circ$

(A squished book)

Orthorhombic

Orthorhombic

$a \neq b \neq c$

$\alpha = \beta = \gamma = 90^\circ$

(A shoe box)

Now, we will go to an area which takes us to the definition of what is a crystal. You may be wondering we have been discussing what is the crystal so far and now I am saying again what is a crystal. The reason why we again go back and ask a question like this is to see that we have 7 crystal systems; they are decided by the nature of *a b* and *c* and the inter-axial angles.

We have also said that there are atoms inside this the point group symmetry and the space group symmetry will tell us how many atoms are there inside this unit cell for example,. So, there may be depending upon the restrictions we put on each of these crystal systems; the number of molecules inside the unit cell will change. We can have one type of molecule, we can have two types of molecules we can have n types of molecules in a triclinic system still with z is equal to 1; that means, the entire assembly of all these molecules need not have any symmetry; still the crystal may crystallize in a triclinic system and therefore, it is a crystal.

So, if you want to determine the structure of it we have to determine the positions of every one of those atoms. So, in a monoclinic system there is a minimum twofold symmetry; we can have any number of molecules any number of atoms, any number of different kinds of molecules different kinds of atoms. So, that is what is meant by a crystal; the crystal now consist of the distribution of atoms and when we talk about distribution of atoms we talk about actually the way in which electron density distributes itself to various atom sides.

So, now comes the very idea of an atom; an atom we always identify with respect to a sphere; that means, in the sphere we put certain amount of you know we have the nucleus we have the electrons surrounding it and so on. But essentially we characterize it by the number of electrons which it carries; the system carries. And that is done in terms of what we call as atomic number in the from the chemistry point of view; we have a periodic table and in the periodic table we have various elements carrying so many of these atomic numbers.

So, H equals 1; hydrogen has 1 atomic number, oxygen has 8 and so on ; that means so many such; so many electrons are associated with these atom. So, as the number of atoms increase, the atoms become more and more dense. The volume of the atom is something which is determined based upon the nature of the nucleus and the surrounding electron density which goes around it.

If we look at an isolated atom, but in a crystal we do not have an isolated atom; we have connected atoms and these atoms therefore, or bonded to each other. So; that means, there is a certain amount of electron density which gives from the atom to the next atom; the atomic electron density is shared.

There is a lot of theory which has been developed over the years which talks about these bonding features. It defines various kinds of bonds and therefore, the density is shared between these atoms, but for our practical purpose of looking at the structure determination and also eventually as you will see when we do X ray diffraction; we are going to assume that these atoms are like billiard balls; they cannot be deformed. So, when we have a carbon we associate 6 electrons with a carbon, the 8 electrons with a with a oxygen and so on and with hydrogen there is only 1 electron.

We also know that these electrons are bound to the nucleus; so we have a central nucleus and the atoms are bound to that except for the case of hydrogen there is no core. We call that as the core the electrons that are distributed are distributed in various levels and we know by atomic theory; how these electrons get distributed into various shells. We have the K shell, we have the L shell, we have the M shell, we have the N shell and so on.

So, these atoms therefore, go and sit inside this box in wherever they feel like depending upon the nature of bonding and the symmetry that controls where they should sit. We have so far seen the symmetry that controls where they should sit with respect to the space groups we have to say the 230 ways in which the atoms can arrange themselves. But it does not tell us what kind of atoms can arrange in what way. And since we have a choice of very many atoms in the periodic table; more than a 100 and way in which they can bond to each other is also different from each other.

For example, we have the ionic species which can form ionic bonds, we have covalent bonds, we have metallic bonds, we have different kinds of bonds. So, all these can occur inside the crystal and that that is the one which gives the property of that material and therefore, we have to see how these electron density is distributed inside the inside the box. So, effectively we have to take the box and dissect the box we have to cut the box into different sizes and different shapes or whatever and then look at the individual pieces.

So, effectively if you want to see what is the inside a box; suppose you get a present in your Christmas is going on now. So, if suppose you get a Christmas present which is in a box what you do you; open the box you open the box remove all the packing material and eventually you find the object which you want to find. Now can we open a crystal and see like that? Obviously, not and if can we see the atoms; we cannot see atoms because the atoms are of the size which will not allow us to use this light with which we see things; we can see only objects which are of certain dimensions. And its so atom happens that atoms do not fall into these dimensions they are much much much much much smaller.

Say for example, we can see an elephant very easily, but we may not see an ant moving on the surface of the back of the elephant because that is very very small. So, if you can use a lens and go to the near the elephants and then look at the back of the elephant and focus the lens; so, that we will see the ant on the back of the elephant. So, in order to see objects therefore, we need lens; now this lens is the one which makes small objects to become large.

So, in laboratory for example, one uses microscopes; so, you can use a microscope to see what is there inside the crystal. Now if you use a microscope to see what is there in the crystal again the microscope uses light. Now the crystals are of the dimension of 1 Å and so we were should be able to see what we want to see in the dimension of an Å; not in the dimension of 5000 odd Å which the light is made up of.

As you all know that we have the wave particle duality we initially in the case of Newton's; Newtonian laws we study the light as though it is made up of particles. And then the wave theory brings in the quantum mechanics where we study this in terms as waves. So, we can talk about matter waves and things like that. So, it is not the intention of bringing in quantum mechanical aspects here except to say that if we want to see the atom we should use a probe. Because we cannot just cut the crystal and destroy it; we do not want to have the crystal destroyed, but still determine the structure of the molecule inside the crystal.

So, if you want to do that we need a probe; now whenever we want to probe something we need a lens as I already mentioned and in order to use the lens we need the light. So, if what is the light which corresponds to the size of an atom; if we look at the electromagnetic spectrum and examine the electromagnetic spectrum carefully, the light which can be of the 1 Å size corresponds to X rays.

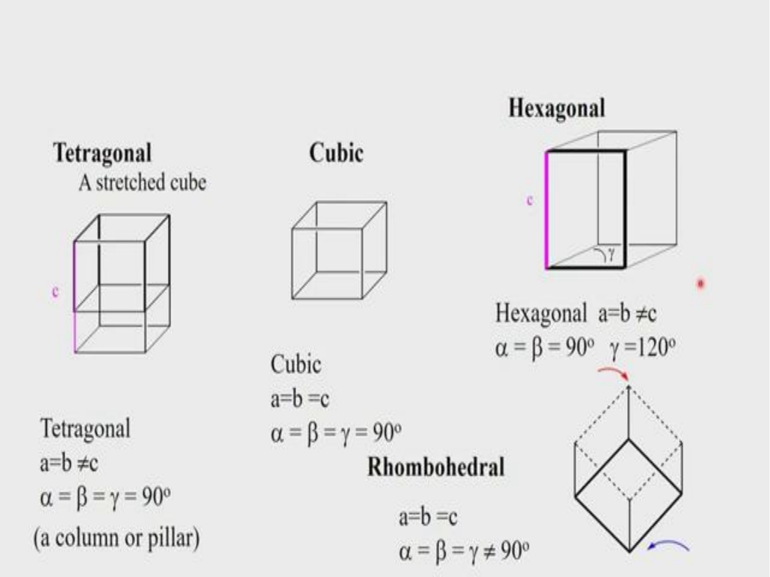
So, X rays therefore, or the radiation which have the wavelength of nearly 1 Å; it could be 10 Å something in the range of 1 to 100 Å or in the range of 0.5 to 100 Å. So, one can use therefore, the X radiation in order to see what is there inside; so, we send the X radiation into the crystal. Now when we send the X radiation into the crystal the X radiation are coming from a rarer medium and entering a denser medium and then they are emerging out again back into the rarer medium ok. So, there is a little bit of physics which we have to learn here in order to understand the process and that process is the fact that process is called scattering.

So, we send in the light it happens in light scattering; we will study the way in which light scattering occurs and the way in which the scattering can be reconstructed into the image of the object inside. So, these examples will tell us that we need a probe and therefore, in this particular next set of lectures; we will look at X rays as the probes which will look into the inside the crystal.

When they look inside the crystal; for example, let us say we had the power or the vision of X rays suppose I have a X ray vision ok; then I can see inside the crystal. And if I see inside the crystal I will see the individual atoms I will see how they are connected to the various molecules. I will see the presence of symmetry and I will see how the 2_1 screw axis is relating 1 molecule to the other if there is a 2_1 screw axis inside.

So, we have to therefore, also determine the symmetry information. So, we not only have to determine what scattering is coming out and so on we also need to understand the symmetry that is contained inside the crystal. So, to understand what is there contained inside the crystal we need the diffraction experiment done. I am using the words like scattering, diffraction very freely today, but all these will have to be defined in a proper physics manner so that we know the physics behind the whole thing and that will form the next few lectures as we come along.

(Refer Slide Time: 20:22)



Tetragonal
A stretched cube

Cubic

Hexagonal

Hexagonal a=b ≠c
$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$

Cubic
a=b =c
$\alpha = \beta = \gamma = 90^\circ$

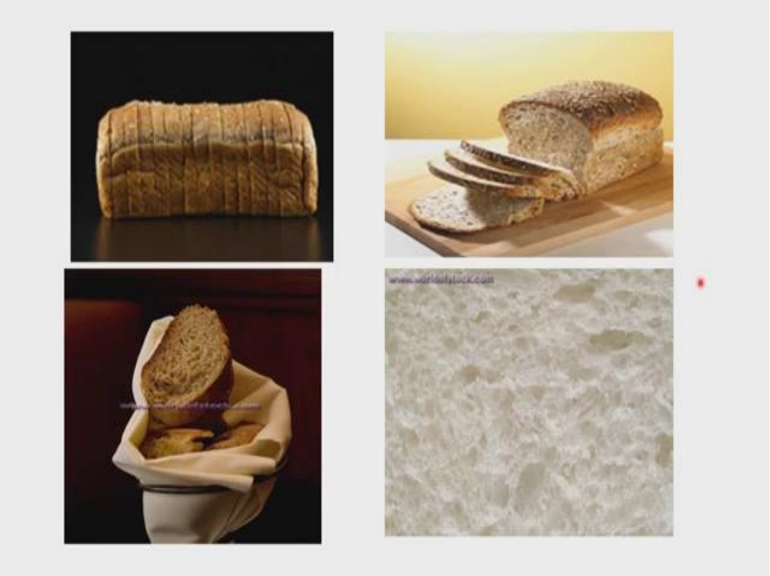
Tetragonal
a=b ≠c
$\alpha = \beta = \gamma = 90^\circ$
(a column or pillar)

Rhombohedral
a=b =c
$\alpha = \beta = \gamma \neq 90^\circ$

So, what we do today is that we have the 7 crystal systems so, how do we look into the 7 crystal systems? One of the ways to look into the 7 crystal systems is to do the job of a surgeon. So, if there is a surgical blade which can cut the crystal to atomic sizes; then we can cut the crystal and see where the atoms are and then find out which atom is what for example, oxygen, carbon, nitrogen, bromine. So, if you have a surgical knife which will allow for us to cut at 1 Å level, then we can take the crystal and cut it.

So, what I will do is towards the end of this section; I will bring in the discussion on how we can cut it; one of the easiest ways in which to understand that is to see the loaf of a bread.

(Refer Slide Time: 21:09)



So, you have a bread loaf here and this bread loaf which you normally buy in a bakery; you see that you have the unit cell here, you start from this as the origin, you have a *a* direction; you have a *b* direction and you have the inside *c* direction.

So, it is a 3 dimensional box; it is in fact, if the bread you buy in the shops is orthorhombic. Sometimes it is tetragonal also, but most often than not it is orthorhombic because somehow orthorhombic is the one which has attracted the attention of many bakers in earlier days I do not know why, but it is orthorhombic. It can have different shapes as I have shown here; it can have a shape like this it does not matter which shape the bread slice is.

So, we have therefore, a unit cell and now we say this is 0 0 0; then this will be one unit along *a* direction. So, this will be the position of the coordinate 1 0 0; then we have 0 0 1 and 1 1 0 all 3; I mean the *x*, *y* and *z*; *z* directions. We can also now take the diagonal along this direction and we will see now that *z* direction is 1 1 1.

So, in the next set of discussions we will discuss how the crystallographic planes come up and how the crystallographic directions come up. So, what we see here in the case of a loaf of bread is that the loaf of bread is 1 unit here; suppose I cut this at half the position I know you can slice it whichever way you want. You can slice it along the 1 1 1 direction; then you will get a nice triangular piece. If you cut it along this direction you will get pieces along the *a* direction, if you cut it like that you will get it along the *b* direction and if you cut it the third direction you will get the *c*.

So, if you cut it along the *a* direction and take the central piece it will be half the distance of *a*. So, the coordinate of this point is 0 0 0 the coordinate of this point is 1 0 0, the coordinate of the half point is ½ 0 0. So, now, let us say we cut this piece and take it out then that particular piece will represent a plane because it is a 3 dimensional object; we take this plane out your bread slices which are like this here which is shown here in this slide or individual planes. So, they are they are a 2 dimensional object.

So, this 2 dimensional plane at half the position we call it as 2 0 0 at one third position we can call it as 3 0 0 and so on. So, these values of 1 0 0; 2 0 0; 3 0 0 now are given to the planes. So, when we say that we are looking at a 2 0 0 plane; that means, we are looking at a plane which is at half distance along *a* and that slice which comes out with *b* and *c* values being 0 and we call it as 2 0 0; this is also called the Miller indices. We will look at it in more detail when we discuss further on the way in which we can now cut the unit cell.

So, when we say we cut the unit cell; in principle we are now trying to see take out the individual planes and see what is there inside that individual plane. And if atoms and molecules and so on are distributed inside this unit cell therefore, when we do this cutting operation and look at that particular slice, we should be able to see what is there in that slice. It could be a part of an atom, it could be an atom itself or it could be several other parts of different atoms. So, how are we going to see it? That is something which will now excite our curiosity and we will keep this curiosity in mind until the next class.

I want to show you one more thing this is just something which is very patriotic to me; this is this is what do you think this is? You all think that this is the slice which has been taken out and placed on the plane of the projection because you may see this is let us say the so called 2 0 0 plane. In fact, if that it is possible that it is a 2 0 0 plane and wherever the atoms and molecules are, you will see these openings and holes and things like that. If you go to a Ayengar bakery for example, and by a special bread this special bread will have all these additives; he will add cashew, he will add badam, he will add this raisins and so, on; the way he makes the bread loaf is actually he makes the dough and when he makes the dough he mixes all these ingredients.

Let us consider these badam then cashew and things like that as possible atoms different kinds of atoms depending upon whether we are adding badam or cashew or some other ingredient different kinds of things can be added. And now when we mix the dough he does not know where they are and then he puts it into the bakery and bakes this into the oven and bakes the bread. When the bread comes out we do not know where these pieces have gone and when we cut this slice it may so happen we may cut a piece of cashew, we may cut a piece of badam and things like that.

So, this if you consider as the 2 0 0 plane; the half point and spread it around like this then you see that these holes are the places where let us say badam and cashew and other things are there. So, parts of atoms; it is not the full atom parts of atoms can be associated with this. Now can we just look at it like this and see whether we can determine the structure a big question mark. It may not be possible because we do not know how many electrons are still associated with these little pieces that only will tell us the nature of the atom.

So, what is in fact, necessary therefore, is to study all the planes and all the contents of the planes put them together integrate them and see what comes out. Now before we conclude the, this particular session; I will also tell you that, this is not the picture of the slice of bread; this is in fact, the first picture taken by our lunar probe sent by ISRO. So, it so happens that I have some contacts with ISRO people and one of them sent me this first picture which was taken when our probe was about to crash land on the moon.

So, this is at a certain reasonably large distance from the moon, but you see this is the moon surface. Very interesting the moon surface and a piece of bread loaf bread slice; they look alike. What is important is that these holes and the way in which it is jagged shows the peaks and the valleys which are present on the surface of the moon. So, this is in fact the picture surface of the moon taken from a closer distance from our lunar probe. I think we will close this at this moment.