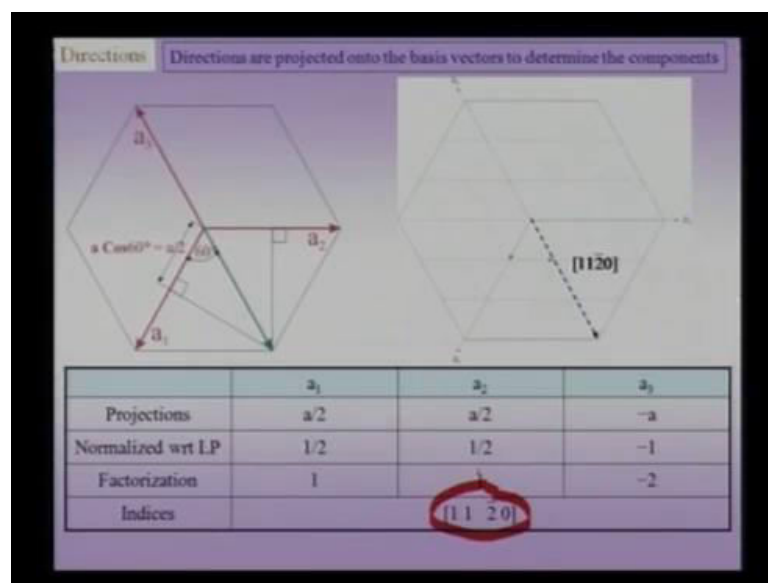


Structure of Materials
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Lecture - 14
Miller Indices
Crystal Structures

To understand miler braving this is for directions.

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We will take up this example as before, as in the case of planes will have 4 indices, the third index being rudiment index in the plane. So, let me show projection of the basal plane, and consider three basis vector plane a_1 , a_2 and a_3 , and let us try to derive the indices for this green vector in this miler braving system. You can see that this green vector is in the opposite direction of the a_3 vector, the way I go by determining the miler indices for the direction would be I would take the projections along the a_1 direction a_2 direction.

And, so the projection along the a_1 direction would be $a/2$, along the a_2 direction would be $a/2$, along the a_3 direction it is results at minus a it is in the opposite direction. And as before I would factor out all the factors with respect to latish parameters, in this case the latish I write the parameter along the 3 direction on the plane or equal, which is

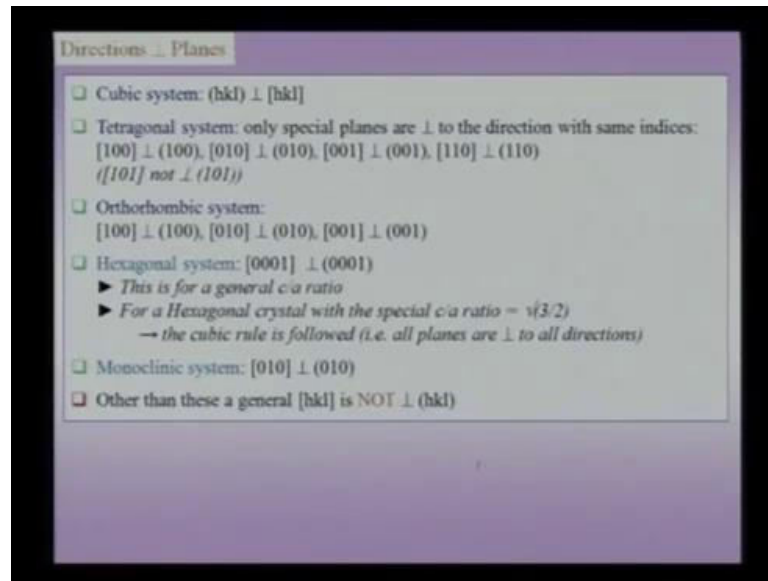
equal to a . And this is one of the important things we already noted about Miller indices that we never leave the lattice parameter.

That means, we never get irrational numbers with respect to indices because, a single lattice parameter a for instance could be 1.7 Å. But, I do not include those kind of units here and therefore, analyses with respect to the lattice parameter, again the value is half half minus 1. Then I factorize this factor half out like you did for the planes, so I would get $1\ 1\ \bar{2}$, and as before I would enclose them in the square brackets to indicate that it is the indices direction.

So, the Miller indices for this direction would be $1\ 1\ \bar{2}$ and the c direction it is 0 because, it never travels along the c direction. So, let me go through the procedure again for this green vector, I draw the green vector and use my three basis vectors on the basis plane I type my projection along the a_1 and a_2 vector, and also the a_3 vector. But, as you can see that I do not actually have to take the projection along the a_3 vector, because, I can derive them from the first 2 indices.

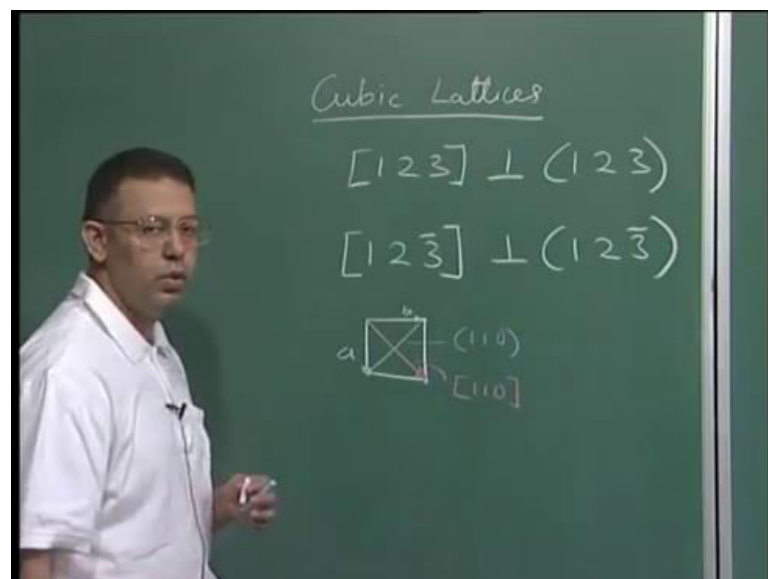
Like here the h, k, l is h plus k , so h minus 1 plus 1 which is minus 2, so I do not have 2 actually determine this indices which is the redundant index. So, I find the projection are along these two directions a_2 by 2, a_1 by 2 and minus a_3 I normalize with respect to the lattice parameters, common take out the common factors and finally, write down the indices without any commas and putting the negative signs. So, this is how I determine the Miller indices for the directions.

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Now, we have briefly mention and there was the question regarding this that what directions are perpendicular to what plains. And in the simplest case which is cube a case we found that any hkl plane is perpendicular and equal to a hkl direction, suppose I take a 1, 2, 3 plane, then the 1, 2, 3 direction would be perpendicular to the 1, 2, 3 plane, so we write this term.

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So, correspondingly any other kind of direction for this suppose any one choose any 1, 2, 3 bar direction, this will be perpendicular to 1, 2, 3 bar plain. But, when we go to lower

symmetries systems, we have to be little careful about what planes are parallel to are perpendicular to what directions. And in the tarragon system there are only special plane which are perpendicular to some special directions.((Refer Time: 04:22))

So, for instance the $1\ 0\ 0$ planes are perpendicular to $1\ 0\ 0$ direction, the $0\ 1\ 0$ is perpendicular to the $0\ 1\ 0$ the $0\ 0\ 1$ is perpendicular to the $0\ 0\ 1$ direction. Then there of course, special plane they are $1\ 1\ 0$ is perpendicular to the $1\ 1\ 0$ plane for, but for I cannot generalize this, the $1\ 0\ 1$ direction is not perpendicular to the $1\ 0\ 1$ plane and, so this is obvious because, suppose I am taking the projection.

So, this is my 4 fold direction of tetragonal system, and now my for indices $1\ 1\ 0$ plane. So, this a x axis a direction this is my b direction and I am taking the projection along the c direction. So, this is my $1\ 1\ 0$ plane, my $1\ 1\ 0$ vector direction would be this, and you can clearly see like $1\ 1\ 0$ direction is perpendicular to the $1\ 1\ 0$ plane. But, this is not true for all the other kind of planes including $1\ 0\ 1$ direction is not perpendicular to the $1\ 0\ 1$ plane.

Because, there is a c elongation or a c contraction in the tetragonal system, in the ortho system, we find the even lesser number of plane perpendicular to the even lesser. ((Refer Time: 05:54)) So, only the three orthogonal basis vectors and there play corresponding planes are perpendicular to each other, so the $1\ 0\ 0$ direction is perpendicular to the $1\ 0\ 0$ plane, the $0\ 1\ 0$ direction is perpendicular $0\ 1\ 0$ plane and $0\ 0\ 1$ direction is perpendicular to the $0\ 0\ 1$ plane. And if we have general $h\ k\ l$ plane it will not be perpendicular to the $h\ k\ l$ direction, so this has to be obsolete clear.

In the hexagonal system, one obvious choice were the direction is perpendicular to the plane is the basal plane the $0\ 0\ 0\ 1$ plane, which is perpendicular to the $0\ 0\ 1$ direction. So, since I have the model of hexagonal system I can show you that which direction is perpendicular to what for this indices one special crystal may rotate the system, but never the less this would have the example.

So, I have this basal plane which is $0\ 0\ 0\ 1$ plane and my $0\ 0\ 0\ 1$ direction will be the direction, which is perpendicular to this plane. So, this is how are a interesting note would be this is of course, this rule is the only plane being perpendicular direction is for the general c by a ratio. That means, I chosen orbit hexagonal crystal, which any given

orbit c by a ratio, then this indices are true I have only one plane which is perpendicular to one direction.

But, there are special hexagonal crystals with special system c by ratios, and this is for instance we choose hexagonal crystal or hexagonal latish root 3 by 2 as see by ratio, then you have the cubic rule which is to be followed. So, this kind of special kind of crystal are called pseudo cubic crystals because, they have the cubic rule been followed, and ratio is often refer to as the franks ratio were in root 3 of course, being the length of the body diagonal of the cube, and the root 2 being the length of the phase diagonal.

So, it is root 3 by 2 and if and my hexagonal latish as this crystal has c by ratio, then I have cubic rule I have followed. In the mono clinic system the $0\ 1\ 0$ is perpendicular to $0\ 1\ 0$ plane, and has you go even lower symmetric once you note that in general, you cannot assume that $h\ k\ l$ plane will be perpendicular to the $h\ k\ l$ directions. So, this is in general true and expect there are some exception for the cubic tetragon orthogonal you can external systems, were we identify certain plane which are perpendicular to certain directions. So, therefore, we are to be absolutely clear and we have to play lot of caution in an understanding that what kind of crystal system or what kind of the latish we are dealing, and then make our conclusion regarding perpendicularity of directions of the planes. Next we come to an important the law, which is it is called ways zone law.

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Weiss Zone Law

If the Miller plane (hkl) contains (or is parallel to) the direction $[uvw]$ then:

$$hu + kv + lw = 0$$

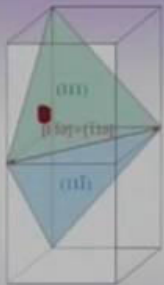
This relation is valid for all crystal systems

So, the way zone law states if a miller plane $h k l$ contains the direction $u v w$, then $h u$ plus $k v$ plus $l w$ is equal to 0. So, I am talking about general miller plane $h k l$ and talking about general plane $u v w$, then if this direction lies in this plane, then $h u$ plus $k v$ plus $l w$ is equal to 0. And of course, when I say lays of course, we know that miller indices the plane can be the direction can always been translated parallel to itself and therefore, the condition would still hold good. And the important thing is the this relation is valued for all the crystal systems, now to understand this relation let us take up a solved example which are also clarify some of the points about this planes and directions.

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Solved Example Find the Miller indices of the intersection of (111) & $(\bar{1}\bar{1}\bar{1})$ planes in a cubic crystal

Graphical Method



Analytical Method-1
Weiss zone law states that if a direction $[u v w]$ is contained in plane $(h k l)$ then:
 $hu + kv + lw = 0$
 Let $[u v w]$ be the intersection of $(\bar{1}\bar{1}\bar{1})$ and (111)

$$\left. \begin{array}{l} (\bar{1}\bar{1}\bar{1}) \Rightarrow -u - v + w = 0 \\ \& \\ (111) \Rightarrow u + v - w = 0 \end{array} \right\} \Rightarrow \begin{array}{l} w = 0 \\ u = -v \end{array} \Rightarrow \text{the indices of the direction are of the form } [u \bar{u} 0].$$

 As miller indices are written after factoring out common factors the miller indices are: $[1 \bar{1} 0]$ or the opposite direction $[\bar{1} 1 0]$.

And in this case I am talking about cubic system, in which I am trying to find the intersection of the $1 1 1$ plane with the $1 1 1$ bar plane. So, I want to find the miller indices of the direction, which is intersection of these two planes $1 1 1$ and $1 1 1$ bar, now we have to remember there of course, when I am talking about $1 1 1$ plane I am talking about set up planes. But, still to make sure that I considered the appropriate plane not the parallel transaction.

So, that they exist in the unit cell which I am describing, so that I can keep my intersection in the first unit itself. So, you can clearly see I have chosen one of the set of parallel plane, so that my job in hand becomes simplify, so I will use one graphical

method and two analytical method to solve this problem of the intersection of the $1\ 1\ 1$ plane in the cubic system with the $1\ 1\ 1$ bar plane.

Graphically; however, it goes the $1\ 1\ 1$ plane and then I could of course, draw the $1\ 1\ 1$ bar plane in the unit cell below this or the same unit cell or the unit cell behind for the simplicity I have drawn the unit cell, right below it to make in a visualization simple of course, I could have also drawn a it within the same unit cell. So, you can see the $1\ 1\ 1$ bar plane has intersections 1 along the x axis, so this origin somewhere here my origin her and this is my x axis and y axis z axis.

Therefore, it intersect one along the x axis, one along the y axis the and minus 1 along the z axis. So, graphically you can see that these two planes the blue plane and green plane intersect along this line, so; obviously, as far as the miller indices goes there are two choices. Either this direction or it is negative and both are solutions to this problem of intersections of these two planes. So, as the direction go there are two direction the line of intersection of course, s will be one line which is the red line.

Now, once I know the line I can find it is direction I suppose take this is the origin I take this as the head of the direction, then I know vertices of this $1\ 0$ and this will be $0\ 1$. So, I subtract $0\ 1$ from $1\ 0$ I get $1\ 1$ bar 0 and therefore, I show in the bracket the opposite direction is best by taking negatives. So, I will get 1 bar $1\ 0$ as the opposite direction, so the line of a intersection would be 1 bar $1\ 0$ or $1\ 1$ bar 0 . So, this a is a graphical simple method of the finding out the intersection of the two planes.

Now, to illustrate the utility of the wave zone law and sometimes it is simplicity, let me solve the same problem by using the ways zone law. Let me assume that if the direction is $u\ v\ w$, and it is contained in the plane $h\ k\ l$ according to the law it is $h\ q$ plus $k\ b$ plus $l\ w$. In this case I know both the $h\ k\ l$ planes what I do not know is the direction $u\ v\ w$ right. I mean this are both these $h\ k\ l$ planes have the direction are common the such $u\ v\ w$ direction.

But, it is the direction which I am trying to determine from this the wave zone law, so the $u\ v$ direction let $u\ v\ w$ be the direction of intersection of the 1 bar $1\ 1$ and 1 bar 1 bar 1 bar plane of course negative of this planes which would of course, not alter me arguments, just in which the kind of point which I am trying to make that sometimes I

would like too considered, the opposite set of plane and whenever I am taking about planes, we are always set of planes.

So, as far as the intersection with respect to the $1\bar{1}1$ plane it is $u - v + w = 0$, intersection with respect to $1\bar{1}\bar{1}$ plane will give you $u - v - w = 0$ solving them simultaneously to right plane find the w is equal to 0 and u is equal to $-v$. So, the indices of direction of the form $u\bar{u}0$ of course, I when write by an indices I always factor out the common factors, so I can write it as $1\bar{1}0$. And as a c the negative over the directions also it is valid choice, it will be $1\bar{1}0$.

So, let me go through this analytical construct or the ways zone law method solving once more, keeping in mind that often it is instructive to use the graphical method wherever the possible, in addition to it any of the analytical solution. Because, that gives you a better visualization of the problem, and also for instance when I draw this direction $1\bar{1}0$ I can see what atoms are seating on in this direction, what is the important in terms of this close pack directions is not a close pack direction, all these questions can be answered when I use the graphical method. So, always multiple method of solution not only make sure that you solve the problem correctly, but also help you understanding the important of these plane and these direction with respect to the crystal.

STUDENT: Sir heavy crystals have some planes and some directions, and in some planes and directions some are direction perpendicular to each other, and some are not. But, why this we can find the number of plane which are perpendicular in any crystal are which or not ((Refer Time: 14:36))

In cubic crystals this automatically leads the fact that when I am a taking about $u\bar{v}w$ direction.

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Weiss Zone Law

If the Miller plane (hkl) contains (or is parallel to) the direction [uvw] then:

$$hu + kv + lw = 0$$

This relation is valid for all crystal systems

I can find the angle between the two and I will find that, the $hu + kv + lw$ it is valued it is valid for also cubic crystal also. Because, now the hkl direction will be perpendicular to the hkl plane, and since this direction is now perpendicular to this direction. The hkl perpendicular the uvw direction, which is on the plane I can use a perpendicularity concept to arrive at a similar kind of equation.

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Solved Example Find the Miller indices of the intersection of (111) & $(1\bar{1}1)$ planes in a cubic crystal

Graphical Method

Analytical Method 1

Weiss zone law states that if a direction $[uvw]$ is contained in plane (hkl) then:

$$hu + kv + lw = 0$$

Let $[uvw]$ be the intersection of $(\bar{1}\bar{1}1)$ and $(1\bar{1}1)$

$$\left. \begin{array}{l} (\bar{1}\bar{1}1) \Rightarrow -u - v + w = 0 \\ (1\bar{1}1) \Rightarrow -u - v + w = 0 \end{array} \right\} \Rightarrow \left. \begin{array}{l} w = 0 \\ u = -v \end{array} \right\} \Rightarrow \text{the indices of the direction are of the form } [u \bar{u} 0].$$

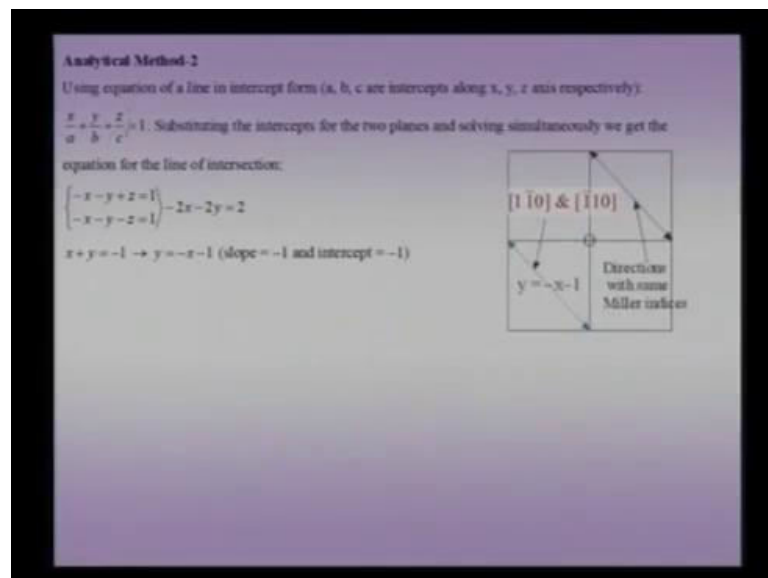
As miller indices are written after factoring out common factors the miller indices are: $[\bar{1} \bar{1} 0]$ or the opposite direction $[1 1 0]$.

Now, let me go through the wave zone law once more, if now my direction is uvw is a common direction between the two planes considering. And I suggest for the sake invert

direction of the inverse signs of these two planes they considering $1\ 1\ \bar{1}$ plane $1\ \bar{1}\ \bar{1}$ plane, and it is the $1\ 1\ 0$ plane I consider $1\ \bar{1}\ \bar{1}$ plane, which is not going alter the solution as I want to show you.

And now I take in the account this direction is common to the both this plains and I apply first plain and then the second plan then I get two simultaneous equations solve them and I get. And since they are three unknown variable in there are two equations I will not get the unique solution from this, but I come to know that w is 0 and u is equal to minus v . And therefore, I can write the indices of the $u\ u\ \bar{0}$, but since if this is true it also true for $1\ 1\ \bar{0}$ which is what the least index I can choose for, therefore, I know my direction of intersection is $1\ 1\ \bar{0}$ or it is opposite direction $1\ \bar{1}\ 0$.

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And in alternate method analytical method to solve the same problem would be to use our common understanding of coordinate geometry. So, here I am going use an equation of a plane for a incense an equation of the plane with intersects along the $x\ y\ z$ direction is given by x by a plus y by b plus z by c is equal to 1 this is an equation of a plane, in the form in which $a\ b\ c$ are intercepts along the three coordinate axis.

Now, I know that are two planes under consideration and I need to find the common direction. So, let me write down substitute the two planes which I have intercept of two planes intercept for r plane; that means, $1\ 1\ 1$ and this is $1\ 1\ \bar{1}$ and substitute them. So, I putting the intercept inside then get two simultaneous equations, and now of course,

I have taken the negatives of those and I didn't get the solution of the common equation, which is $-2x - 2y = 2$ which writing in the different form it is $x + y = -1$.

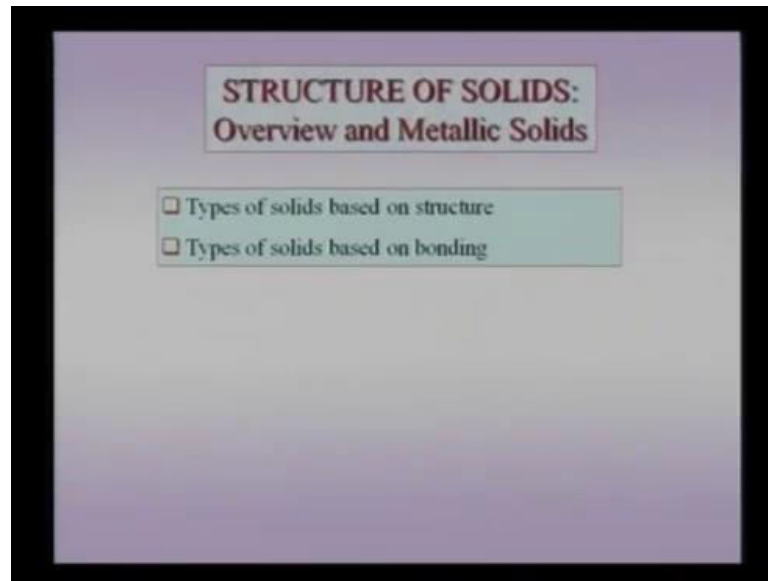
And even for the writing about the different form I will write it as $y = -x - 1$ which is in that typical form of $y = mx + c$, which means that my slope is -1 and my intercept is -1 . So, my slope is -1 and my intercept is -1 along the x direction, so both the x direction is in the y direction slope, intercept is -1 . So, this is I plotted the equation line $y = x - 1$ and since I am talking about directions which are parallel I could even translate and put it here and determine in the Miller indices and determined here it would not matter.

So, I could now write down the Miller indices of such a direction either the positive or the negative as $1\ 1\ \bar{0}$ or $\bar{1}\ \bar{1}\ 0$. So, I have more than one method at my disposal to determine the Miller indices of the intersection, but as you can see each one of them intersect in a certain way. And typically if I have to solve this problem I would use either the graphical method, and also the analytical method, but also you can use your familiar coordinate geometry, which is the equation of the plane in the intercept form.

And then solving there are two planes and then I find the common direction by solving simultaneously; that means, line which is common to both the planes. So, I solve for that and then I write it $y = mx + c$ form plot that equations, plot that line and then find its Miller indices. So, I could do that and I find the same thing that Miller indices $1\ 1\ \bar{0}$ or $\bar{1}\ \bar{1}\ 0$, so with this we come to the end of a set of what I mean to say lectures on Miller indices.

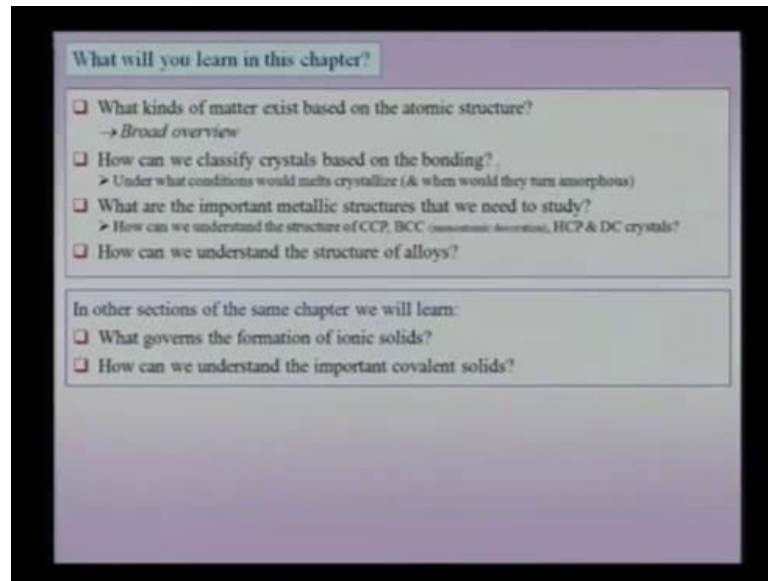
And as I said it is ((Refer Time: 18:59)) Miller indices, but and it is typically used to represent directions planes and we also seen, what are the important planes and directions which we need to keep in the mind, we are talking about the basic crystals. And we will connect with the important some of these when we actually talk about we already being doing some of these already with respect to crystals, but when we really talk about crystals some of these planes and directions, the low index ones are very important with respect to some of these properties. And therefore we need to keep Miller indices language in our mind when we dealing with crystals.

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Next chapter we are dealing with the structure of solids, here we will start with the a broad overview, and then go on to metallic solid before we take up ionic and covalent solids. We shall especially focus on some of the rules formation of the ionic solids we worry about the kind of bonding in this kinds of solids, and some of concepts would just be a revision of something we delta with before. But, special care should be taken when we you are in this chapter because, some of the concepts might look familiar. But, we will be dealing with a additional concepts, and which would be interviewed with the previously existing concepts and therefore, we should not because, some concept seem familiar.

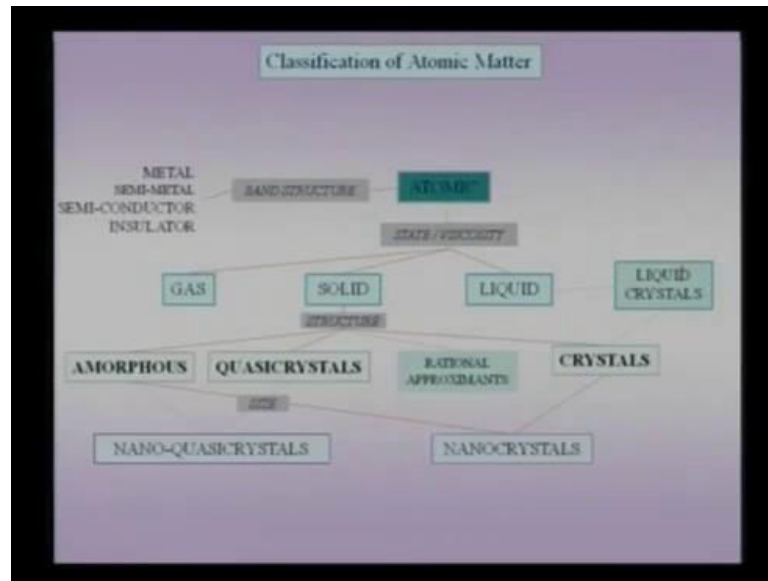
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So, what is the at plant in the chapter we will try to understand how matter are can be classified. And this will be very broad over view and often some of this concepts we will not deal with the elementary course, but is good for a student you know that there are the additional things, and some of us later on we want to worry about these. We would like to know how classify the crystal based on bonding, we already seen about bonding in the materials.

But, this is the specially classification of the crystals based on bonding, and some briefly we consider how things may for instance amorphous or say crystalline. You will then take up some important metallic structures of course, some of which we already consider for in the cubic close pack and the body centre cubic etcetera, then we will try to understand the structure of poleis, especially the concept of ordering and disordering in a alloys, and later we talk about ionic solids and covalent solids.

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So, talking about the classification of atomic state of matter, we can even use the band structure of classification, were in we know material can be classified as metal, as a semi metal, as semi conductor or a insulator. So, this is purely from the band structure point of view, and in this course of course, we are not going to detail in this accept, but we should note that suppose I am talking about the state or viscosity aspect of the classification atomic state of matter then I have familiar gas solid liquid picture.

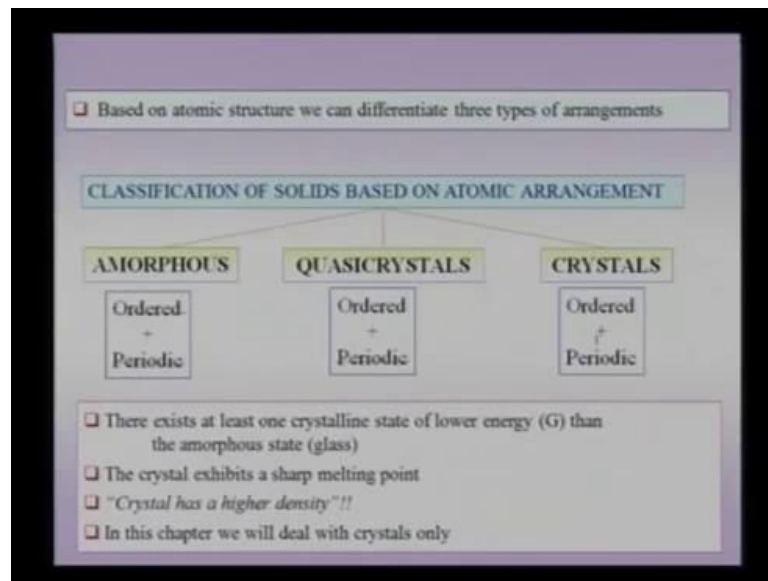
Further what I am interested in this particular course is a structure solid, and if you look at the structure of solids on one hand we will see that there is concept of crystal which we are dealing with quite a bit, so far. On the other extreme the concept of amorphous such materials, in other words which are totally disorder, there are other structure possible like things between liquids and crystals, which can be called liquid crystals. We will again not deal in too much depth and this course about liquid crystal, but it is worth wide node there are state of matters which are between liquid and crystals.

And often our language of crystal of grapy of our understanding of the atomic structure, can be extended various way to in cooperate liquid crystals. In fact, but of course, they also oppose new challenges, and the new kind of defect can be formed in this kind of liquid crystals. Often we are taking about classification not just based on symmetric, which are now talking about crystals, but we are also taking account in the size in which

case often people talk about nano crystals where in grain size or one of the atomic entity size is very small.

Now, this course we will not deal with depth with a another form of matter known as queasy crystals, but it is worth wide to know there are states of matter which are queasy crystal which are dishing from crystals and also which are distinction from amorphous states of matrix.

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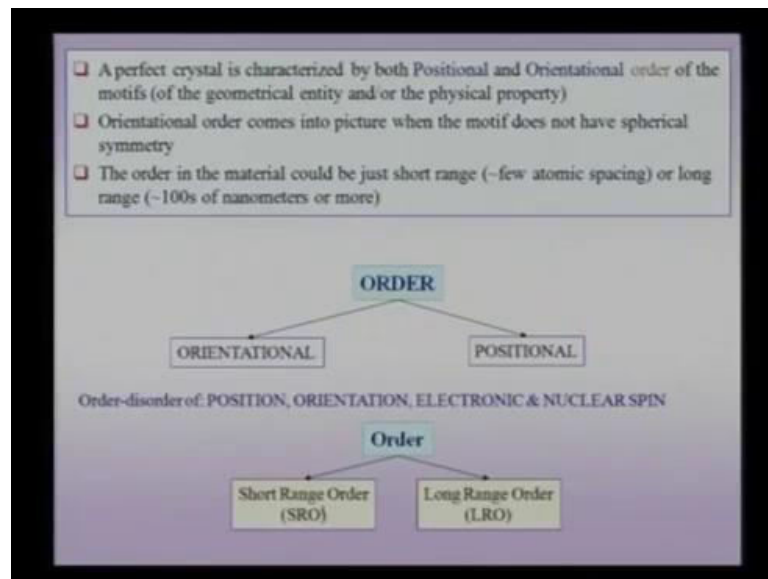
Now, what characterizes this three important state of matters in the solid state the atomic based on the atomic arrangement, we are talking about crystals which are order and periodic. And of course, we already given a very formal definition of a crystal based on the latish plus motive, but we know they have the characteristic that they are order and periodic. Amorphous structure are neither order nor periodic and of course, we also saw examples were in we could seen in some position order.

But, there was no orientation order and put together the position and orientation order we call them amorphous structures. Quasi crystal have a property that they have order, but they are not periodic, and often such a structure is some time called quasi periodic structure. But, this course will not take us into detail into the queasy crystals, but it is important to note, there are this kind of additional structures which are often associated with this allowed crystallographic symmetries.

That means, quasi crystals can not only have allowed crystallographic systematizes, but can also have the disallowed crystal symmetries. But, all of them do not have any kind of periodicity, it is important to know that the typically the stated crystalline state and unknowing the comparing may crystalline state with the amorous state. So, assuming that I am comparing my crystalline state of the amorphous state for say a martial of the given composition.

Then it is stated that at least there is one crystal which is lower free in energy then the amorous state. So, therefore, if I have a amorous material and sometimes the term glasses also used, it will be noted that such a martial would want to crystalline, so that is the important point to note. Certain aspects of crystalline you have already know that they have the sharp melting point, and also have an higher density than the enormous phase constructed of the same composition. In this chapter we will mainly deal with the crystals, but in the passing we will also talk about, conditions under which amorphous structure can form.

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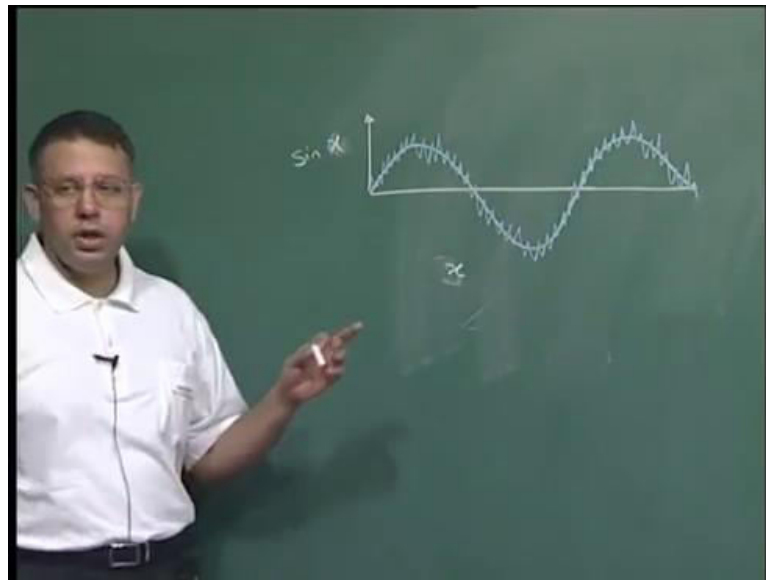
We have already noted that crystals is characterize by both positional, orientation order of the motives and the which can be a physical property or a geometrical entity. This perhaps we not introduce, so far it is the range of the order, often the order we are talking about could be the complete long range order, which means the entire material providing

across the entire material perhaps or the smaller entity. But, defiantly much larger in the length scale compared to the atomic entities we are talking about.

But, there could often be just short range order, and this is something important note and we will see that there could material which have long range order. But, no true short range order they could material with the short range order, but no true long range order and all these possibility exist. And therefore, we should need clear that what kind of an order we are talking about when a dealing with the kind of crystal, to understand for instance give you us some of the simplified examples.

It is often found very difficult or contract in to understand that how can we have long range order, but no short range order it is easy to understand we can have short range order, but no long range order. So, this is an simple concept to understand by the reverse that how can I have long range order, but no short range order, it may come as a surprise that every single crystals we have a nature. That means, any single crystal be a produce actually has short range it is order and actually has only long range order.

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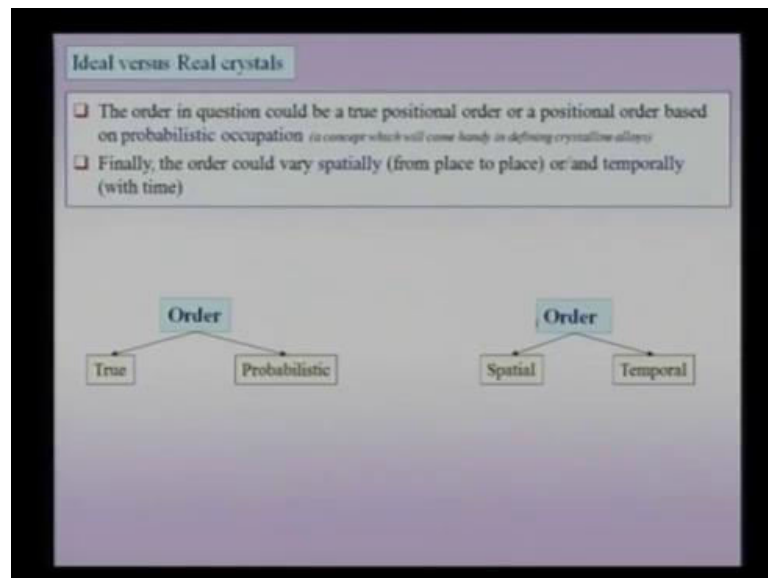
This is something we should note, but I will explain using a simple mathematical example. Suppose I have a sign wave which is my ordering function is for the sake, so now, this is my very well order function say $\sin x$, so I am plotting, so this is my sign theta and I will say this is my theta or x . Now, suppose on top of it, so just to make sure that I am going to x to infinity I will put x instead of theta.

So, now, this is the perfectly order function in the long range, now suppose I overlay some kind of noise on top this function. So, let me take the different color to illustrate that noise even though there is lot of noise as for as each point is consider, you can see that they over all long range order is obvious to u right. So, this is the example where is the short range disorder; that means, I am talking about length scale this small rage I will not find any order.

But, in the long range ways I find the order, in fact, in real crystals at any finite temperature you know there is the thermal vibration; that means, atoms are vibrating around the atomic positions. Therefore, in the short range if I finish my time picture, then I will see that know atoms to be located in the satisfy, so there is short range disorder, but we known crystals still have the longer range order.

So, since a this was a point which seems constraint u reword first site, I want to explain this aspect that you can actually have short range disorder, and still have a long range order. Of course, you can even thing of a situation where in a short range disorder and long range quay periodic order, but we will not deal with those kind of situations in this course.

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We aspect of orientational position order we have already talk about, but we will take up some more examples to see how we can understand this crystals, we will introduced one more concept, the concept of probabilistic order. So, for we have talked about

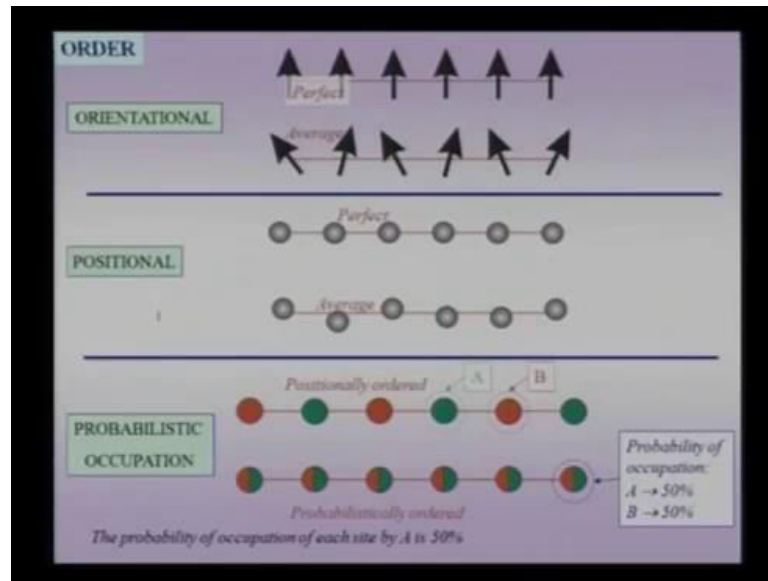
orientational order in positional order, but we take up another kind of an order which is known as the probabilistic occupation. Now, we will actually take up a examples and this particular concepts and probabilistic occupations based order would very useful in describing disorder alloys.

And one more concept regarding when we are taking about order is a we can taking about temporal order or special order. So, this is again something which we have to keep in mind typically, so for were are been taking about spatial order, but we are seen suppose I am taking about liquid spatial order keeps on varying will see that for a liquid typically have the short range order, but the short range order is not fixed in times.

So, there is an reason where in I could find for instance atom some kind of a quad essential which is order for since an quad essential quardi national cell. Then as different point of time these atoms will break up part in go make a different kind of a short range order region. That means, the temporal picture is vary, but the same short range order could be found in one region initially, then a different region in a latter on, so the time picture is varying, but if an take a single time picture.

So, of snap shot then I would see that I can have the short range spatial order and liquids. So, I would again have to, so though some of these concept may not be immediately relevant, but it has I said we are starting with broad overview of all the concepts, then we will use all the concepts are relevant for studying or immediate crystal or the simple one we are going to deal with.

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So, when I am talking about true order probabilistic order this is perhaps illustrative slide which will put in perspective, what I mean by orientational order, positional order. Orientational order in the true sense, orientational order in the average sense, positional order in the true sense, positional order in the average sense and finally, probabilistic occupation order in the true sense or how do I define in my probabilistic occupation order.

So, this example of crystal we are seen before were in a set of arrows which are at it is latish points all order perfectly. Now, this kind of thing we obviously you can see it is positional and orientation order crystal the one of the top, now this could be for instance picture of all the magnetic sense aligned in a Ferro magnet within the domain. So, I could get the picture like that, but then suppose you would see that both heats such as a material, then you could see the slowly some of the Spence my gets disorder.

Never the less you would see that there is the net magnetization in the material and therefore, I do not want to through away my concept of the crystals. Suppose, I strict definition of the orientation order and strict orientation of positional order, such material below will not be classified as the crystal. Because, now orientation order is that we are position order, but still as you can see most of the arrows are pointing upward.

So, in the average sense it is still orientation order, those are not as perfectly as the crystal at the top, but it is still order to a large extension. And I do not want to throw

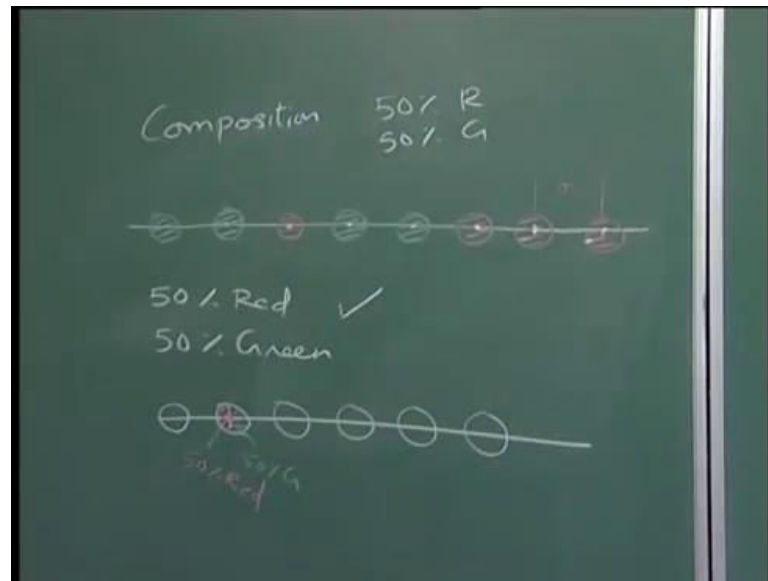
away all my crystallography are all the description using of this crystallography, so I will deal with this as an average crystal or a crystal with average orientation order.

The positional order similarly can be perfect as you can see here, since these are spherical entities. So, I do not have to talk about a circular entity, I do not want to talk about an orientational aspect of this kind of a crystal. Now, in the average since you can see that some of these atoms are spheres or circles or not exactly sitting at the lattice point and somewhere around the lattice point. But, you can see there within certain a region of space of the lattice point, so there are still order in the average sense.

So, this is the picture I was giving for instance thermal vibration, so any instant of time for instance atoms may not be sitting at this point they may be away from the lattice point. But, still in the average since there around the lattice point, so even in this case I can consider this as an average positional order crystal, so I can have true orientational order or an average orientational order are true positional order or an average positional order when I am describing crystals.

The third description the probabilistic occupational description is perhaps the interesting very full when we are describing is the disorder alloys. So, I can have a true disorder system, where in as you seen this would be lattice point one dimensional crystals for instance with the two dimensional lattice. Now, my lattice point should be the centre of these red circles, and my lattice points will be one red circle and one green circle. Now, this system could get disorder, so let me draw one possible disorder of this kind of a system on the board. So, that we understand that what is that we are describing here.

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So, as you can see in the order systems we had half in the number of green, circles and half the number of red circles. Now, so let me I have randomly put some 4 red circles, and 4 green circles, and you can clearly see here that if I have to treat it perfectly in terms of my language Christology, this is the amorphous structure. Because, there is no unit cell and if I go little further here 2 green see a separated by a 1 red later on I am here there are 3 red separated by 2 greens they could be another red or a green here they could anyone.

But, I am over all putting 50 percent of mine see as in red, and 50 percent has green, so let me shade them. So, I have a array of points for a instant I could have array of points which are spaced a , and randomly I put 50 percent red, 50 percent green circles on those points. Truly speaking in the true language I have a disorder structure, which I would called amorphous. That means, it is not a crystal, but I will introduce this concept call I am talking about probabilistic order.

That means, I know because, I have a composition which is 50 percent a say for instance 50 percent red and 50 percent green. So, my composition is, so it is clear the composition 50 percent red and 50 percent R and 50 percent green, so I can make I know if I take any random point, there is a 50 percent chance of finding a are 50 percent chance of finding b. Therefore, I can describe the structure here saying that at each latish point or each point.

Now, I have a probabilistic occupation my 50 percent green, so this is green and this is 50 percent. So, each point there is the probabilistic chance that I find a or b 50 percent, so this kind of a probabilistic picture is what I am introducing, I have drawn the probabilistic picture I get the picture as shown at the bottom of this figure. When I draw a each point occupy wide by 50 percent a or 50 percent b.

Now, what is the structure on the top this is the crystal a perfect crystal, which is positional a of course, order which as a lattice parameter for instance the red to red distances a for instance or if I take this picture it will be $2a$, I am taking as a length here to here then it will be $2a$. Now, the lattice is probabilistically order crystal in the row was a bottom crystal is only a crystal, only the probabilistic sense, in the true sense it is anonymous, what is the lattice parameter of this it is a , it is not $2a$ right.

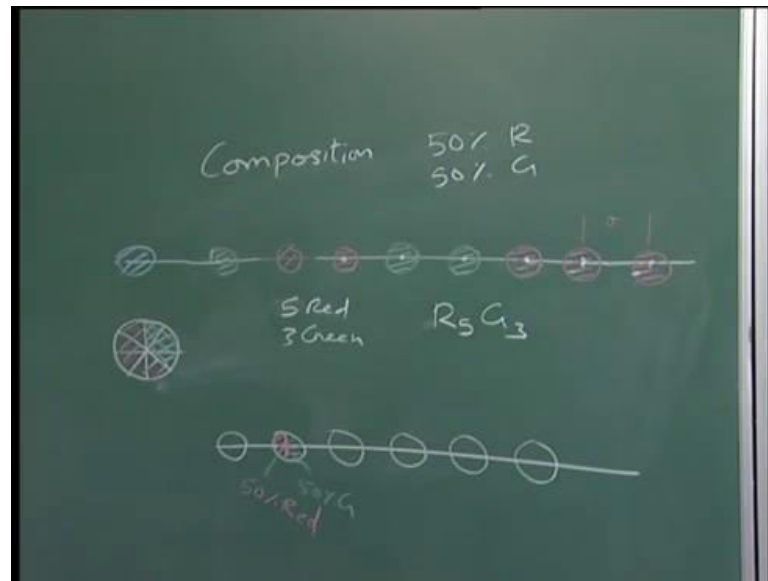
And each side is now occupy by a motive which is forming this crystals, which is now not a half a red plus half a green that is not the right description of this motive. Because, you cannot suppose the real atom and I cannot cut half a green atom realistic to another half a red atom and put it in each lattice point that is not the picture I am showing here. There is the 50 percent of probability of finding the red atom and the 50 percent of the probably finding the green atom.

Of course, you could have a entity when there is three atoms, they could be 4 different entity you could be dealing with. So, when you have instant of two entity for instance you could have many, many entities, and it could have all disorder crystal and you would then still use the language of crystallography, nothing that no I define the crystal based on probabilistic occupation, so many had a question.

STUDENT: ((Refer Time: 39:16))

The question has may a got is that do any to have 50 50 percent composition or it can be any composition or I let me add some more to the question. Then there will be more element what I am describing here, which I was mentioning, so; obviously, the composition could be anything.

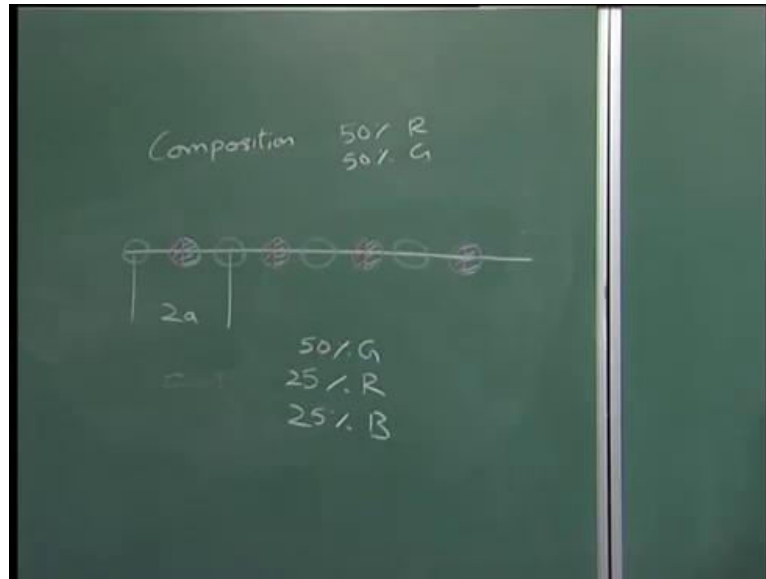
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So, instead of having suppose in the same example, suppose I had putting have make one more of it, see in this composition I am going to make. So, for every 3 plus 2 5 red have 3 green. So, my composition would be red 5, green 3, so my sphere the probabilistic sphere now would be or the probabilistic circle now would be not be equally divided. So, I will have to be divide 5 by 3 8 parts, which I am perhaps can do it, so 8 parts to my circles, and my chance for finding green is 3 1 2 3.

So, I will mark 3 of this in green and the remaining which is 1, 2, 3, 4, 5 is my correct, so this is my probabilistic occupation of a single lattice point. Of course, instead of having I could add one more entity like a blue entity for instead to this whole picture, so now, my crystal constraints green, red and blue, and they could be completely disorder for instance. So, I need to add some probabilistic for the red presence of blue also, which would be some part of the circle probabilistic occupation. Further interesting possibility exists is that suppose I have three elements as before like in the case of the blue and green.

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So, this is the kind of picture we have in a torsion matrix, it is 50 percent green, 25 percent red, 25 percent blue right. So, let me write the down here, 50 percent green, 25 percent red, 25 percent blue one of the sub lattice is completely order, this sub lattice were in the green entity is completely order. So, green seat in perfectly lattice positions, but the second sub lattice is now probabilistically order with respect to the red's and blue's.

So, if I take one particular region of space were in this crystal existed, how would see for instance this could be red, this could be blue, this could be blue, this could be red, but so that half of this these position occupy of half in red and half in blue. So, now, I have a description of crystal with 2 sub lattices, one sub lattices fully order with green, the other sub lattice being order is probabilistically with respect to the red and the blue. So, this is the possibility and, in fact, you often find in crystals were in one sub lattices is completely order, the other sub lattice disorder with respect to 2 atomic species, which in generally ((Refer Time: 43:24)) three atomic species.

STUDENT: Sir, if we consider this probabilistic occupation description then if you can consider any percentage does not mean that any amorphous material can be described as a crystal.

Very good question very, very good question, now the question is that let me refresh kavitha's the question, the question is that, if any percent any composition can be

accommodated by a probabilistic picture into the crystal and frame work, contain a very amount space as crystalline. What is the starting point of all over the crystalline picture, complete positional, complete orientational order, right in amorphous structure there is no positional order, we have been taking very special cases, were in the special order, but one of the order does not exist I call it as amorphous as very special sense.

But, general amorphous structure domain class, then there is no position order, under this circumstances I can even associate an average position to any of these structure or an average probabilistic occupation, so that is not possible for all structures. What is very special circumstances and therefore, what I want to do I do not want to call this as a amorphous structure. But, I still want use my language of crystallography which can be done.

As you can see there are still there are the position where located and often find a or b and at the local mode scale, suppose these where real atoms then you obvious notice that the local region should be disorder. Suppose one of the spheres big one small, then the region which are too big spear could be spread apart compared to the region which is one small are too small more sphere file. But, what I am doing I am therefore, I am talking about probabilistic occupation here I have taken equals a circle which is not that case with real atomic materials you will have never two different atoms at same size.

Therefore, there will be atomic distortion at the very local scale, but we average them also out and we say that we talk about long region where in I can describe in it terms of average lattice parameter. So, this is a also becomes and average lattice parameter that thing has to kept in mind, but these are important question, which we were in mind when your describing this kind of crystals.

STUDENT: Sir, I have one confusion, suppose the region polymer where is equal what part we get which we can comfort and I have calculated I have got some in the, but most of the percentage call this is the enormous material, so what is the cut line of percentage of this.

So, here we are asking Mr. Patel as a most sophisticated kind of questions, how do I go by describing percentage crystallite. Especially in more complicated systems like polymers, now polymers themselves are long chain molecules and typically they never become fully crystalline. So, we have to often describe this kind of crystal in terms of

percentage crystallite, I think these are much more advance question at this stage, so maybe we will take up at a later stage when we are actually in a position perhaps when we have the all the 2 crystallography and the 2 average ordering and our control.

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With respect to the range of order various states of matter can be understood as in the table below

Range of Spatial Order

Short Range (SRO)

Long Range Order (LRO)

Class/ example(s) ↓	Short Range		Long Range	
	Ordered	Disordered	Ordered	Disordered
Crystals/ Quasicrystals	✓		✓	
Glasses/ Liquids ^a	✓			✓
Crystallized virus ^b		✓	✓	
Gases		✓		✓

Notes:
^a In practical terms crystals are disordered both in the short range (thermal vibrations) and in the long range (as they are finite)
^b - Amorphous solids
^c Other examples could be: colloidal crystals, artificially created macroscopic crystals (a picture in the next slide)
^d Liquids have short range spatial order but NO temporal order

Again let me give a broad overview of some of this status matter which we have come across various kind of crystals, and amorphous things and we will try to compression in terms of the short range order, and the long range order. So, in this table for instance I have got crystals, quasi crystals I have classes, liquids we can have the biology entity like crystallize virus and gases. And if you want to compare the short range order with an long range order.

Some of the easiest one to do are the crystals, here and as a pointed out I am talking about order. Now, in still in the in some sense in the perfect order of for mathematics sense, we are still not relaxed our order sum of the description we have seen just now I am talking about some mathematical sciences. So, I can see the one extreme would be crystals and quasi crystals you have order in the short range and in the long range.

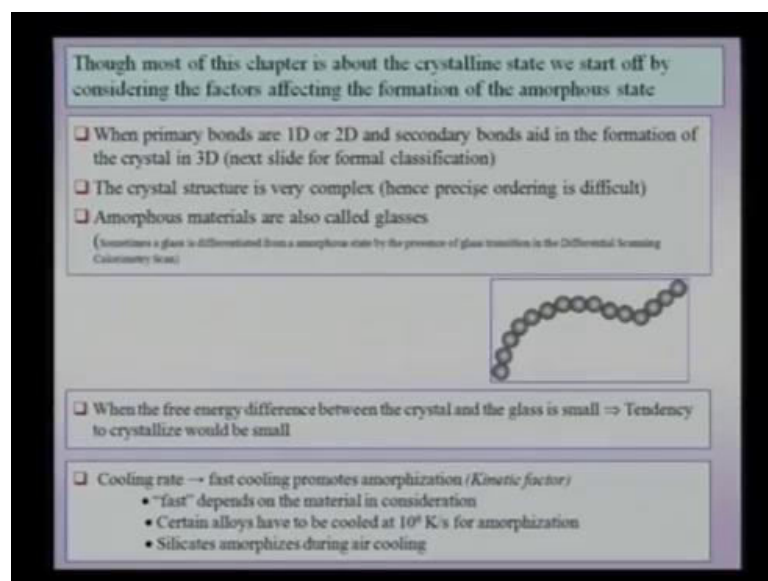
And the other end would be gases which or neither the order in the short range or in the long range. So, gases these are the extreme were in of course, we already know that they do not even have any kind of temporal order, the temporal order always change. Crystallize a virus for instant and there are the examples in this class like collide crystals,

artificially microscopic crystals, some of this like and they would come under this class like the crystallize virus, they are disorder in the short range.

That means, that within the virus entity there is no order, but or no order in the real sense we are talking about here. But, they could be order in all these virus entities could be order into long range crystals, this glasses and liquids and when we are talking about liquids we know that liquids have short range special order, but no temporal order. So, glass, so I am talking about the snap shot picture of a liquids, which can be compared to some sense to a glass were the short range order, but no long range order.


So, therefore, we can see that the various kind of entities which are order in the short range or disorder in the short range. And the special class which we are dealing with the detail here are the class of crystals, which order and in the short range as well as the long range. So, you should keep that when we studying this other kind of material, and other kind of possibilities and often, these are equally interesting possibilities.

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Though most of this chapter is about the crystalline state we start off by considering the factors affecting the formation of the amorphous state

- ❑ When primary bonds are 1D or 2D and secondary bonds aid in the formation of the crystal in 3D (next slide for formal classification)
- ❑ The crystal structure is very complex (hence precise ordering is difficult)
- ❑ Amorphous materials are also called glasses
(sometimes a glass is differentiated from an amorphous state by the presence of glass transition in the Differential Scanning Calorimetry Scan)



- ❑ When the free energy difference between the crystal and the glass is small \Rightarrow Tendency to crystallize would be small
- ❑ Cooling rate \rightarrow fast cooling promotes amorphization (*Kinetic factor*)
 - "fast" depends on the material in consideration
 - Certain alloys have to be cooled at 10^6 K/s for amorphization
 - Silicates amorphizes during air cooling

Though we are as pointed out the we are dealing mostly with the crystalline materials, and we would, but still we would like to know under what circumstances would I form a crystal. And in other words what are the opposite of those circumstances which will lead for the formation of the enormous of the glassing state.

So, when primary bounds are one dimensional are two dimensional and secondary bounds 8 in the formational crystal. This kind of condition is preferred for the amorphous state, and if a crystal structure is very complex and; that means, that precise order is very difficult, again you tend to form amorphous structure. These amorphous materials as I sometime told are also called glasses, the distinction often is made by the presence of glass transition.

And some materials you would notice there is actually digesting glass transition position, which can observe in differential scanning calorie materials scan or they could be have material any would you see this distinguish glass transition where in crystallize position take place before for the glass transition can take place. When the free energy between the crystal and the glasses, small then the crystallize would be small, there are kinetic factors which is promote the promotion of glasses for instance of fast cooling rate could be for time formation of glasses.

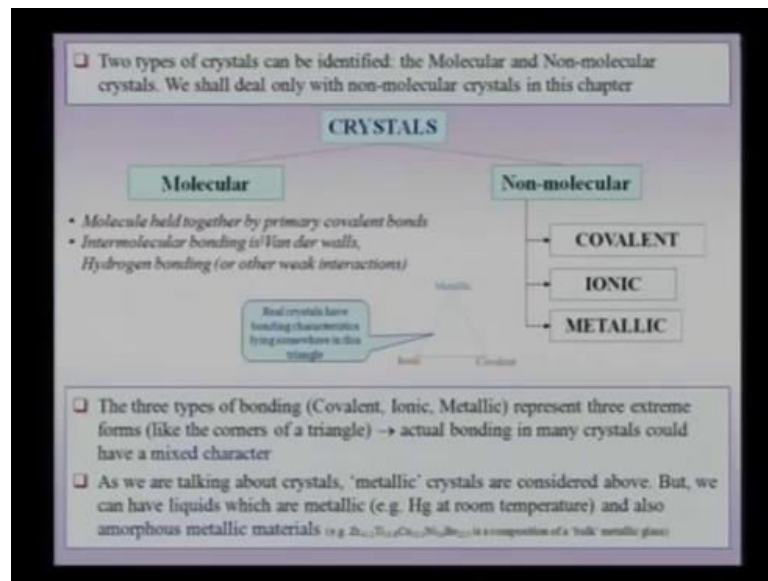
Because, you do not enough time for the formation of crystal very we in require precious ordering. If you want to cool certain alloys form glasses which would be safe and metallically then you need to use employ very high cooling rates, like 10 per 6 Kelvin per second, which can be use by method known as plate pulling or by taking actually of a past cooling rotating copper wheel, and throwing the motive pull of metal of top factor which is called milt spinning.

But, there are other materials like silicates which have an natural tendency to form glass very easily; that means, you taken silicate, material which is the common plate glass material and pull it slowly, and still you obtain the glasses tilt substance. So, though for we never delt with how to form a glass or how to form a crystal, but then we have to keep in mind that even though crystal with respect to any amorphous phase at least there is one crystal which is the global free energy, which is lower than that of the more face.

But, reaching that global minimum may not be easy for instance suppose I can leave by window open glass for zoology time scale is room temperature, and still it may not crystallize. So, there are kinetic factors which come in to play, and that will tell you how easily can I form a crystal, how could be that crystal in terms which quality, in terms of positional and all orientation order. And therefore, the crystal those materials which have poor tendency to form crystals may not be fully crystallized.

And, in fact, they often turn on the amorphous and less special carries taken to crystallize the, on the other hand that would be materials which is crystallize very easily for pure eliminate crystallize very easily. And you want on obtain aluminum in pure form in a amorphous stage, then you need to employ very difficult techniques and it is not easy to form amorphous alumina. So, they are this both extremes and therefore, I need to worry based on this kinetic factor is the quality with of the crystal I have obtain.

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When you want to classified crystals, and this is one particular kind of classification which is often very instructive. As we can classified crystals as molecule crystals and non molecular crystals, now this classification becomes all the more important when we talking about session properties, like melting point and certain other properties, like deformation, behavior, etcetera. Molecules crystals are typically made of molecules, and this molecules formed by typically primary bounds which are covalents bounds.

This molecules then go on to make a crystal using bonds which are much weaker like the ((Refer Time: 53:10)) some other weak interaction. And therefore, the bounding which is responsible for the formation of the crystal itself is a actually very weak bound, and there could off course this automatically implies such in typically molecular crystal have a low melting point, and there is easy to deform and typically they turn out to be very soft.

Because, a bond which is responsible for the formation of the crystal, which is oppose to the bound which is formation for the molecule. And now the molecule itself is the atomic

entity, which is can perform the role of motive information of the crystal that itself cannot be broken down. But, the weak forces which are forming the crystal that can be broken on way easily and therefore, such material have very distinguish characteristics the molecule of crystal compare to non molecular crystals.

You will look at the bounding of non molecular crystals, they could be predominantly covalent, they could be ionic or metallic. And we that remember that typically there of course, examples where in the bounding is almost truly metallic, but in general real crystal could have the bounding characteristic, which lies somewhere in the face triangle of metallic, ionic, covalent.

In others words what I am saying is that, the these three bounding characteristics covalent, dynamics, metallic of the extreme case in extreme forms and actual bounding crystal could have a mixed character. And we will take up some examples of this later on in the chapter, another point to be noted is a though we dealing with classifying crystals, and we are using the word metallic in this contest for instance. We could have for instance metallic, crystals and also liquid crystal metallic you know the mercury room temperature is liquid, but it is its metallic.

And, so to emphasize again we could have function ionic you would have metallic liquids and therefore, we should not confuse this term as restricted only to crystals. So, here we talking about crystals in molecular, non molecular forms and there could be non molecular crystals which have for instance ionic bounding or metallic bounding. But, we could also have liquids which have metallic character, and additionally we could have an amorphous materials which are also metallic character, for instance there is composition here, continue, zirconium, titanium, copper, nickel, beryllium.

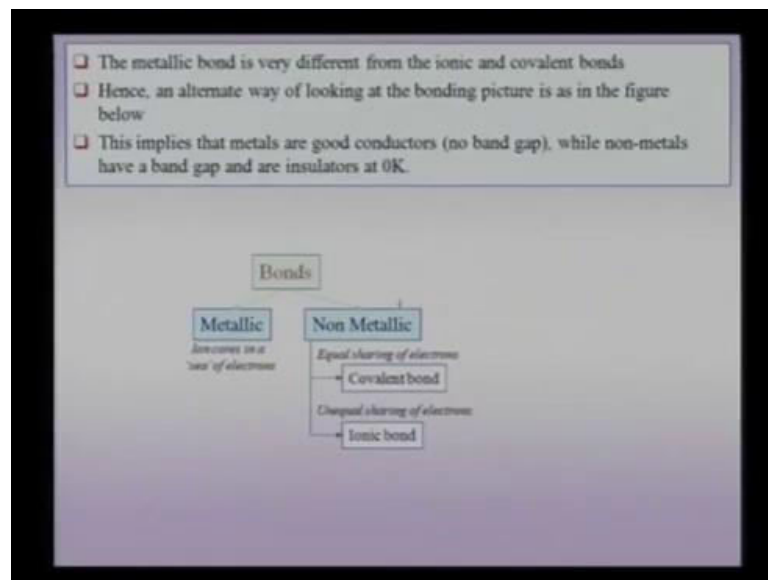
And this composition can be easily form into a metallic glass, which is known as bulk metallic glass. In other words I could obtain microscopic sizes of the this metallic glass by slow cooling, so some of this compositions for instance you can cool at the rate of 1 Kelvin per second or slightly more 10, 20 Kelvin per second and obtain a glass. That means, suppose I take composition like this milted, and pull it to copper mood I can get for instance a glasses material.

Of course, I will not make the copper mode too thick I like to make it some obtain, so that the walls mere by an extra by heat. But, still this materials can easily classified or

made in to bulk amorphous, so I have to remember that crystal can be molecular or non molecular, molecular crystals have primary bounds which found the molecule typically covalent. But, the inter atomic forces or enter molecular of forces which leave to the formation of the crystal are when the walls type the other kind of the interactions.

Non molecular crystal could have covalent, ionic or metallic bounding characteristics, and typical crystal could also have mixed characteristics between metallic, ionic and covalent. And important thing to remember is had we could have liquids, and amorphous materials also which have the certain bounding characteristics, which look in terminology in similar to the non molecular crystals. So, we should not a confuse for incense metallic crystal with the metallic liquid or a metallic amorphous alloy.

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The metallic bound is very different from the ionic and covalent bounds, so therefore, I would like to when I am looking at this sub picture. And we will associates in this whole picture, typically we will be dealing mostly with non molecular crystals, we will not deal with any examples of molecular crystal, though we will take the bound to example with illustrate what are molecular crystal, but typical example would be for non molecular crystals.

So, from the bounding picture I would like to classified the whole picture has metallic, and non metallic crystals. Now, this picture is important to note because, in metallic crystals for instance each elements for instance copper going onto form the metallic

crystal, would take electrons. And these electrons would become form of c of and therefore, each electron now belongs to the entire solid or the entire crystal. While and therefore, there is large scale picture that to the metallic bond, and equivalent bonding, and ionic bonding there is always a local picture which is predominantly important.

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METALLIC CRYSTALS

Are Characterized by:

- Positive ions (*placed in a lattice*) in a free electron cloud
- Metallic bonds are non-directional
- Each atom tends to surround itself with as many neighbours as possible!
- Usually the high temperature (wrt to MP) structure is the open structure (e.g. BCC)
- The partial covalent character of transition metals is a possible reason for many of them having the BCC structure at low temperatures

- FCC → Al, Fe (910 - 1410°C), Cu, Ag, Au, Ni, Pd, Pt
- BCC → Li, Na, K, Ti, Zr, Hf, Nb, Ta, Cr, Mo, W, Fe (below 910°C)
- HCP → Be, Mg, Ti, Zr, Hf, Zn, Cd
- Others → La, Sm, Po, α-Mn, Pu

Though most metals are usually crystalline, by special processing and/or by using special alloy compositions amorphous metallic alloys can be obtained

Now, let us start with the topic of metallic crystal into little more detail, and we will consider the various aspects especially of the common metallic crystals, we know that metallic as crystal has positive ions placed on lattice points in a free electron cloud. So, the word cloud free electron here means sea of electrons, in which these ions are immersed. And important characteristics of metallic crystals that the metallic bond is non-directional, this is an important consequence when it comes to different information behavior and all the properties of the metallic crystals.

Since the bond is non-directional, typically there is a tendency of atoms to surround themselves as many neighbors as possible. But, we will see that this is not a perfect rule, but there is a tendency like that, and you also find again this is not a rule, this is sort of general observation which has exceptions. That the high temperature structure is typically open structure with respect to the lowest temperature structure, just a more close pack structure.

So, this is again a sort of common observations in many metallic crystals, the partial covalent character of transition metals, which take us back to this diagram that actual

bonding in many material need not be purely metallic ionic or covalent. Later on we will see examples of material which have bonding characteristics between ionic, covalent and this case we talking about bonding which is between metallic and covalent.

We see that, this partial covalent character some covalent character in many transitions metals of is suppose reason for many of them having a BCC structure, which is open structure at low temperatures. Typical metals you would notice are having one of these few structures, FCC is the close pack structure and we will take up the many examples later on for aluminum, iron under certain temperature assume and pressure assume copper, silver, gold, nickel, palladium, platinum all have the FCC structure.

And what I mean here is a cubic close pack structure, the BCC crystal common examples are lithium, sodium, potassium, titanium, zirconium, hafnium, niobium and many more. The other close pack structure which metals tend to form or the hexagonal close pack structure, which is beryllium, magnesium, titanium, zirconium, hafnium, zinc etcetera. The other lesser found crystals like for instants we will take about this few examples later on in the chapter.

Like for instance polonium forms the simple cubic structure which is rare example because, typically metals do not form simple cubic structure, they form more lightly one of the these structures. But, polonium forms a simple cubic structure, magnesia can form more complex structures for instance the alpha magazine and beta magazine, can have a very common complex structures. And you will considers the some examples, which I have also these kind of complex structures. But, the more important once at our which will be the focus of presence study will the FCC, BCC and HCP crystals, and we will take up each one of these in lot of detail in this lecture.