Structure of Materials
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Lecture - 21
Chapter - 04
Crystal Structures
Chapter - 05
Defects in Crystals

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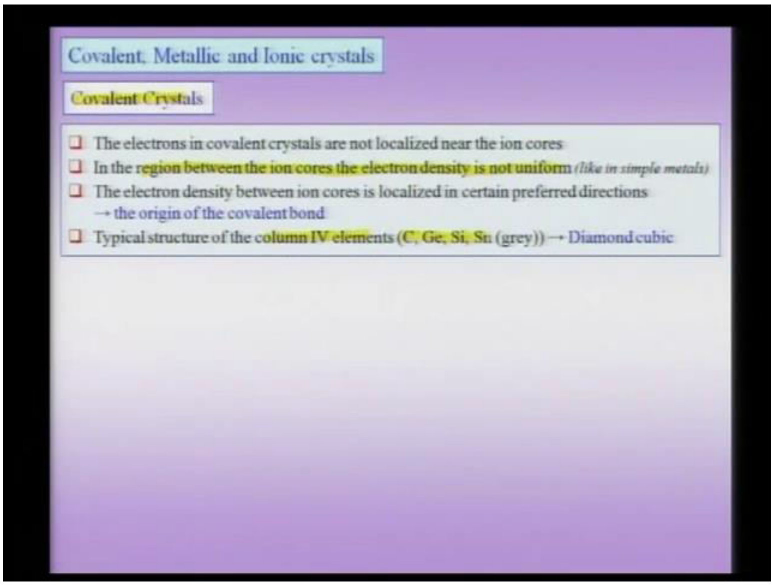

Covalent, Metallic and Ionic crystals

Covalent Crystals

- ❑ The electrons in covalent crystals are not localized near the ion cores
- ❑ In the region between the ion cores the electron density is not uniform *(like in simple metals)*
- ❑ The electron density between ion cores is localized in certain preferred directions
  → the origin of the covalent bond
- ❑ Typical structure of the column IV elements (C, Ge, Si, Sn (grey)) → Diamond cubic

Before we consider covalent crystals. Let us take up revise some of the previous concepts with regard to covalent metallic and ionic crystals especially with regard to the bonding in these crystals. So, let us look at covalent crystals first, we know that electrons in a covalent crystal are not localized near the ion cores. Suppose, we have the positive ion charge near the nucleus, the electrons are not localized there. And in fact the region between the ion cores the electron density is not uniform.

And typically it is like which is the example of uniform density between the ion cores would be a metallic example, but you notice that there is a preferential direction between the ion cores wherein the electron density is very high. This is very simple to look at the picture and understand more than in words. So, the typical structure of column 4 elements for since we know they are these carbon, germanium, silicon and gray tin have a diamond cubic structure.

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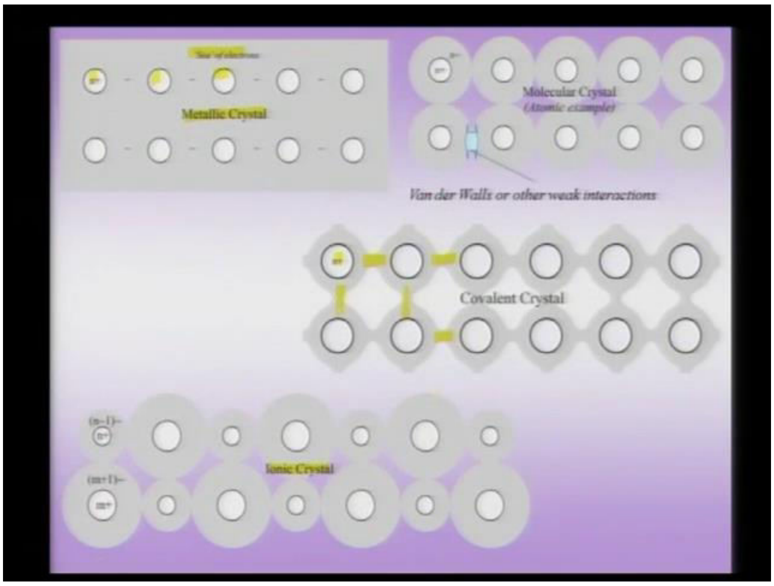

So, let us look at the electron picture to understand how does a covalent bond look. So, you know in a covalent crystal that the electron density unlike a metal for instance this is a metal. And you know that there are these positive ion cores and between the cores the electron which is called the sea of electrons. The electron density is practically uniform of course, there could be some non uniformity, but it is practically uniform. On the other extreme it is a covalent ionic crystal, wherein all the, what you call the charge is localized around the ions and there is not much as in the interstitial region.

The covalent crystal is a special case of this kind of a presence of interstitial electron density and this is as you can see localized along the direction of the bond. So, this is what we typically called the interstitial high electron density is what we call the covalent bond. So, you can see that here between the ion cores. So, the ion cores are positioned here and we have this interstitial region along certain direction that you find the high electron density which we call the covalent bond. And which is in sharp contrast to the metallic crystal where the electron density is uniform or the ionic crystal which is shown below here. Wherein we find that the electron density is localized around the ion cores.

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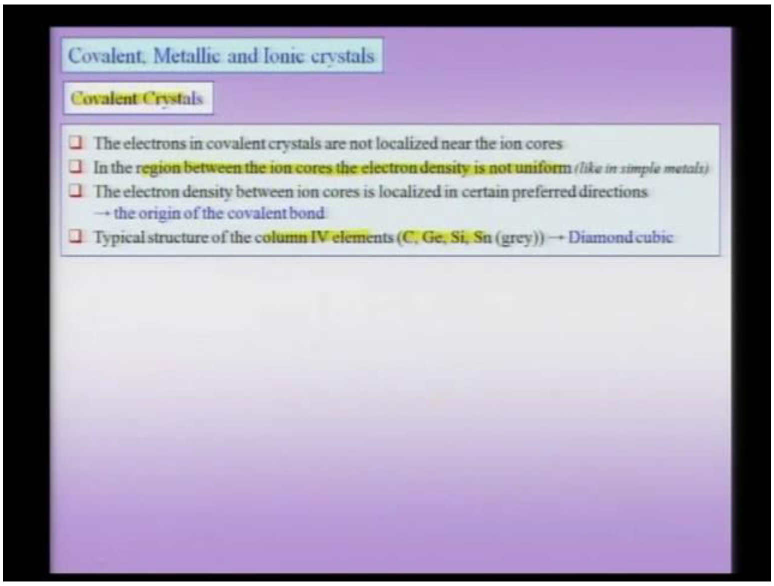

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So, covalent crystals are very different in that sense from metallic or ionic crystals, but then we will also try to understand how we can have a smooth transition from or a continuous or a continual transition from covalent to ionic kind of bonding.

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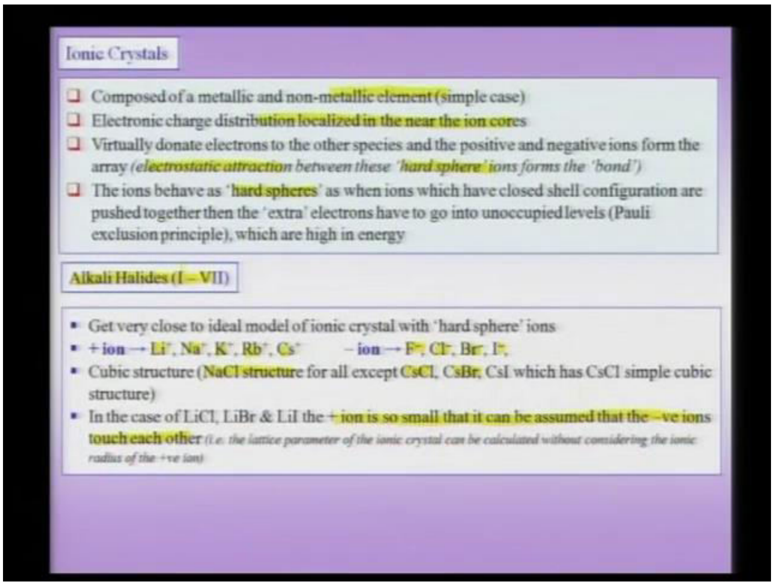

Ionic Crystals

- Composed of a metallic and non-metallic element (simple case)
- Electronic charge distribution localized in the near the ion cores
- Virtually donate electrons to the other species and the positive and negative ions form the array *(electrostatic attraction between these 'hard sphere' ions forms the 'bond')*
- The ions behave as 'hard spheres' as when ions which have closed shell configuration are pushed together then the 'extra' electrons have to go into unoccupied levels (Pauli exclusion principle), which are high in energy

Alkali Halides (I – VII)

- Get very close to ideal model of ionic crystal with 'hard sphere' ions
- **+ ion** → Li^+, Na^+, K^+, Rb^+, Cs^+ **– ion** → F^-, Cl^-, Br^-, I^-,
- Cubic structure (NaCl structure for all except CsCl, CsBr, CsI which has CsCl simple cubic structure)
- In the case of LiCl, LiBr & LiI the + ion is so small that it can be assumed that the –ve ions touch each other *(i.e. the lattice parameter of the ionic crystal can be calculated without considering the ionic radius of the +ve ion)*

The ionic crystals as we have seen is composed of metallic and non metallic elements referred in simple cases. The electronic charge distribution is localized near the ion cores and in this case we can consider the bond as one of these species donating the electron to the other species. So, one of them becomes negative the other one become positive and there is an electro static attraction between the positive and negative ions which we call the ionic bond or the and which in finally, leads to the formation of the ionic crystal.

In the simplest case we can assume that these ions behave like hard spheres, in other words the, if you have a donation of an electron. The electronic configuration is complete this close shell is formed and when another ion is we try to push another ion into the same region then according to the Pauli's exclusion principle. These have to go to an higher energy level and therefore there is a strong repulsion and in the simplest case this kind of repulsion can be thought of an hard sphere repulsion case.

And the closest that 1 gets to a pure ionic crystal are the alkali halides which are formed between the group 1 and column 1 and column 7 elements. Now, we will also see as we saw that we will be talking about 2 important transitions, transition from a purely ionic to a sort of a covalent bond and also transition from the type of bond like ionic to covalent to metallic to molecular kind of a crystal.

So, these 2 kinds of things we will focus now, so in these alkali halides typically the positively charged ion could be lithium, sodium, potassium, rubidium or caesium. And the negatively charge ion which is a single singly charge negative ion could be fluorine chlorine, bromine or ionic. So, you could have an ionic crystal for instance lithium fluoride or sodium chloride which we have seen the structure of before. And these sodium chloride for instance come as close to an ionic bond as possible theoretically.

And in this case you can treat almost the, what you might call the model of the ion as an hard sphere model of the ionic. Typically, these structures we as we have seen for this case of a sodium chloride or all mostly they are N A T L sort of structures, but there are exceptions like for the case of caesium chloride, caesium bromide which we have seen form a simple C s C l kind of structure. So, this a simple cubic structure instead of a phase centred cubic structure.

There are cases in which the positive ion is so small that it can be assumed that the negative ions almost touch each other. And therefore, when we make the lattice parameter calculation we practically ignore the positive ion in making the lattice parameter calculation. So, this alkali halides as I said are perhaps the example of what you might called a nearly perfect ionic bond, wherein all the charge is localized around the ionic cores.

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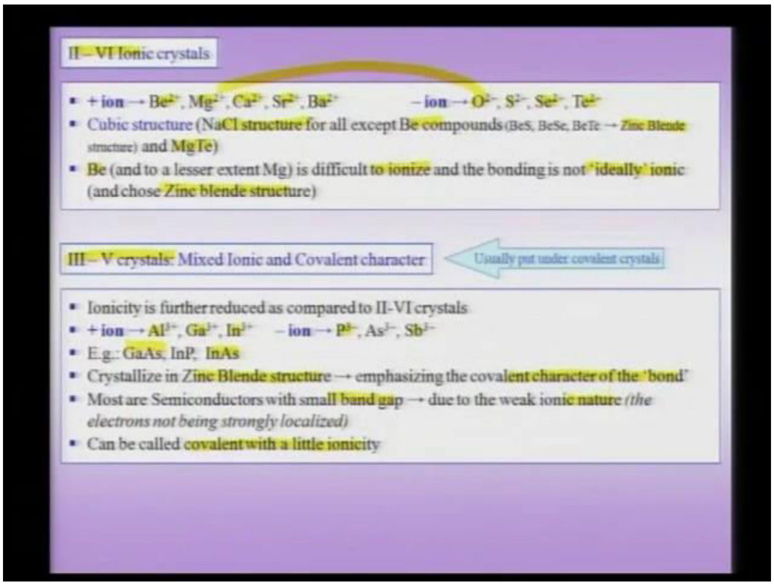

II – VI Ionic crystals

- + ion → Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} – ion → O^{2-}, S^{2-}, Se^{2-}, Te^{2-}
- Cubic structure (NaCl structure for all except Be compounds (BeS, BeSe, BeTe → Zinc Blende structure) and MgTe)
- Be (and to a lesser extent Mg) is difficult to ionize and the bonding is not 'ideally' ionic (and chose Zinc blende structure)

III – V crystals: Mixed Ionic and Covalent character

Usually put under covalent crystals

- Ionicity is further reduced as compared to II-VI crystals
- + ion → Al^{3+}, Ga^{3+}, In^{3+} – ion → P^{3-}, As^{3-}, Sb^{3-}
- E.g.: GaAs, InP, InAs
- Crystallize in Zinc Blende structure → emphasizing the covalent character of the 'bond'
- Most are Semiconductors with small band gap → due to the weak ionic nature *(the electrons not being strongly localized)*
- Can be called covalent with a little ionicity

If you go to the 2 6 column ionic crystals, you will notice that the bond is ionic, but still here it is when you make an hard sphere approximation to the ions. It is not that perfectly obeyed and the for instance the ions which can form this could be beryllium, magnesium the positive ion calcium, strontium or barium, the negatively charged ion could be oxygen, sulphur, selenium or tellurium.

And, typically for instance you could have an magnesium oxide at compound forming. Now this magnesium oxide crystal typically most of these go into the sodium chloride structure, except for these beryllium compounds and magnesium telluride which do not have the sodium chloride structure. And these beryllium compounds for instance they have the zinc blende structure which is telling you as you already seen the zinc blende structure that it is tetrahedral bonding which is dominating right.

That means that the iconicity is slightly reduced, now it is not that ionic as a purely sodium chloride kind of a structure which is true for the previous cases which is the 1 7 structures. So, the 2 4 structure already is what you might call little stretch on the pure ionic character of the bond and you could often see that the structure stabilized is not characteristic of a pure ionic crystal. And you can see that beryllium and is difficult to ionize and the bonding is not ideally ionic and therefore, they choose this zinc blende kind of a structure.

Now, when you go to the 3 5 crystals the bonding is practically now cannot be even called ionic it is typically put under the covalent kind of a bonding and the bonding is what you might call covalent with a little bit of iconicity. So, now, we are starting from pure ionic bond we have transitioned into the 3 5 crystals wherein the bonding is what you might say more covalent than ionic in nature. So, for instance the ions which can contribute to this kind of a formation of ionic crystal is aluminium, gallium, indium which are the positively charged ions.

And the negatively charged ions could be phosphorous, arsenic or antimony and for instance you could have an aluminium, phosphate. And the important compounds here for as you know are many of them are semi conductors or technologically very useful compounds like gallium arsenide or indium arsenide. And these typically crystallize in the zinc blende structure. So, we have lot of important technologically important semi conductors coming out of the 3 5 crystals.

And this zinc blende structure further emphasizes the covalent character of the bond and these semi conductors which form from these typically have a small band gap. And this is because the weak ionic nature and these electrons not being strongly localized. So, as you go even in the ionic crystals as you go from the 1 7 to the 2 6 to the 3 5 compounds. You can see that the iconicity is reducing and slowly that reflects in the kind of crystals which form the kind of crystal structure which is finally, expressed by the combination of ions.

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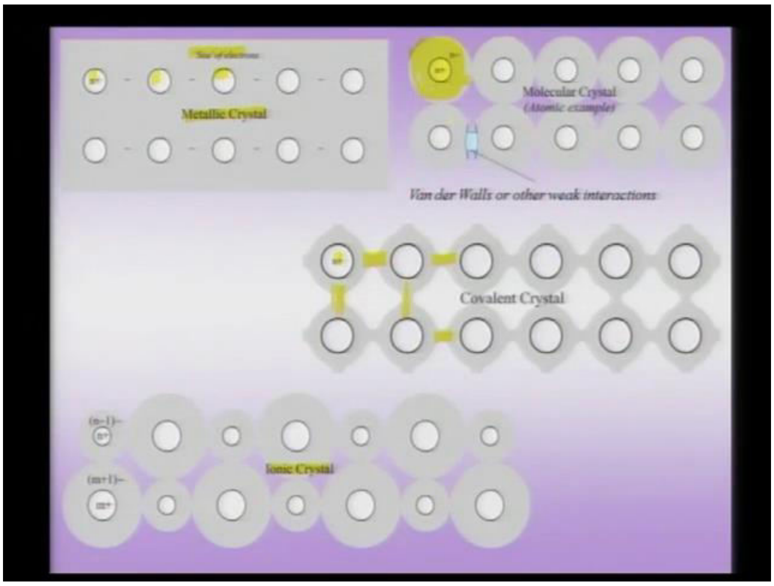

Now, we already seen this picture and we have seen that how the electron density distribution is taking place around the ion cores and in the interstitial region. So, the extremes as I pointed out are the metallic crystal wherein there is a uniformed distributional negative charge in this as we which we call the sea of electrons. The other extreme is complete localization of the charge around ions which is which is in the case of the ionic crystal, but somewhere in between wherein there are directional distribution of charges.

That means, the electron density is not uniform, but this also not localized, but specially it is directed along the ion cores along certain directions for instance in the germanium or carbon diamond structure. You would notice that it is along the tetrahedral directions around a single carbon atom, so that would be a covalent kind of a crystal. Now, we also talked about something known as the molecular crystal and in that case as you know that the that these individual entities of molecules which I am shading here.

So, this would be a molecule for instance and now the interaction between the molecules is of a weak type, this is a weak interaction which is actually leading to the formation of a crystal. So, typically because the interaction which is weak which is giving rise to the crystal the melting point would be lower and this is the characteristic of molecular crystals. So, we will take up at least one definite example in this set of lectures regarding what is a molecular crystal, but we already considered quite a few examples of ionic crystals and metallic crystals. And we will proceed in this set of lectures with the covalent crystals next.

Student: Sir, as we are talking about the crystals. So, these are only can you distinguish between them on the basis of crystal formation.

I am not quite understanding what you mean by soft sphere interaction, but let me guess what I what you mean by a soft sphere interaction. In this case what we mean by hard sphere interaction is what is said here in this slide here.

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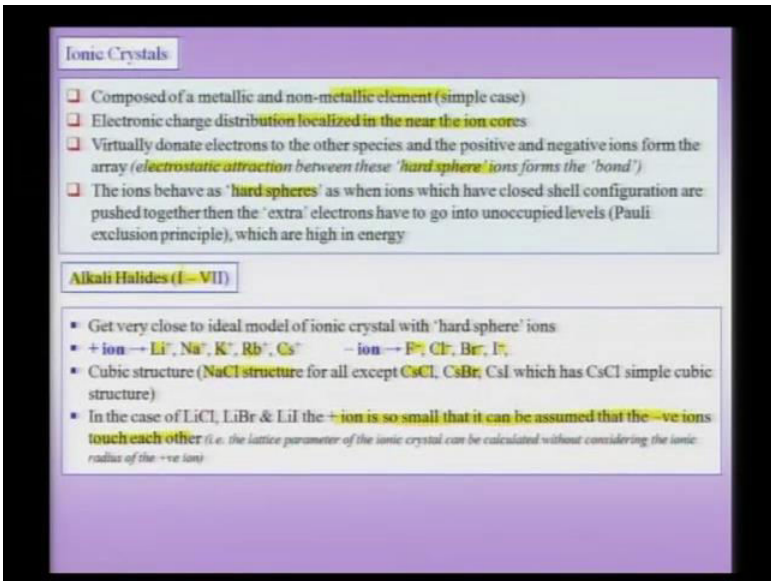

Ionic Crystals

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- In the case of LiCl, LiBr & LiI the + ion is so small that it can be assumed that the –ve ions touch each other *(i.e. the lattice parameter of the ionic crystal can be calculated without considering the ionic radius of the +ve ion)*

In other words if I approximate my ion to be a hard sphere; that means, that there is a region for from which another ion cannot approach. So, for when that is 2 ions are far away it is purely an electrostatic attraction, but when it comes closer it stays an attraction, but after certain distance the repulsion goes to practically infinity. So, this is what I mean by an hard sphere repulsion it is not the kind of 1 by r power 6 or those kind of attraction repulsion cases. So, it is not like.

Student: This is also comes in some polymers soft materials like polymers. So, that is also 1 softened crystals after it they cannot approach each other.

Student: This is already guessed in our particle, but if you consider hard sphere of that is the, I think 2 are similar both things are similar.

I do not know when use a world soft, I do not know what context you are using for instance suppose, we use a soft condensed matter. So, in that context there is some difference between the meaning we are using for hard sphere compared to the meaning perhaps which you imply from a soft material. So, but yeah in many cases you can use an hard sphere approximation for an ion or for a metal and it could work very well for you.

Student: Sir, for consider 1 substance may be ion particle of any particle consider substances, so this stage hard sphere will be ((Refer Time: 12:01)).

Now, the question is that what kind of an inter atomic potential are you modelling? This is what we are asking? Now, suppose I model a inter atomic potential in which I have an attractive region, but the repulsive region is also a certain kind of a polynomial certain kind of a power function. Say 1 by r power n kind of a function. Then there is no problem this is a soft sphere in repulsion and a soft sphere in attraction. So, there is a region of the influence of the 2 spheres, but suppose I model the repulsion. As if it is 0 for a certain distance and infinity for a certain after a certain distance, then that I call a hard sphere model, now at least approximately. Now, to understand more for instance quantitatively what I what is meant by the iconicity of the chemical bond.

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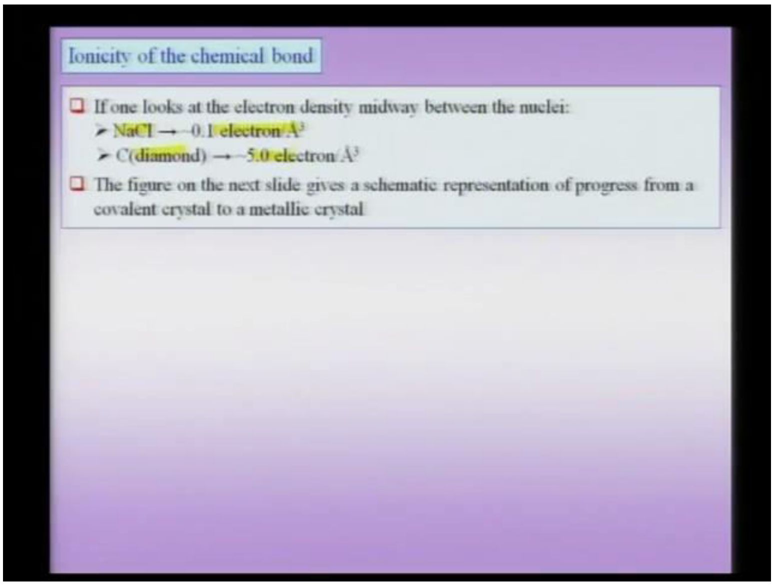

Ionicity of the chemical bond

- ☐ If one looks at the electron density midway between the nuclei:
  - ➢ NaCl $\rightarrow \sim 0.1$ electron/Å^3
  - ➢ C(diamond) $\rightarrow \sim 5.0$ electron/Å^3
- ☐ The figure on the next slide gives a schematic representation of progress from a covalent crystal to a metallic crystal

If you look at the for instance the electron density midway between 2 nuclei, in the case of sodium chloride for instance which is as I said it is a very good example of an ionic bond. The electron density is 0.1 electron per angstrom cube. It is a very small electron density between the ion cores, but in the case of carbon which is assume as a covalently bonded material the electron density is 5 electrons per angstrom cube. So, there is considerable electron density in the inter ionic region in the case of the covalent bond which is clearly seen from the actually, considering the electron density between the 2 ion cores.

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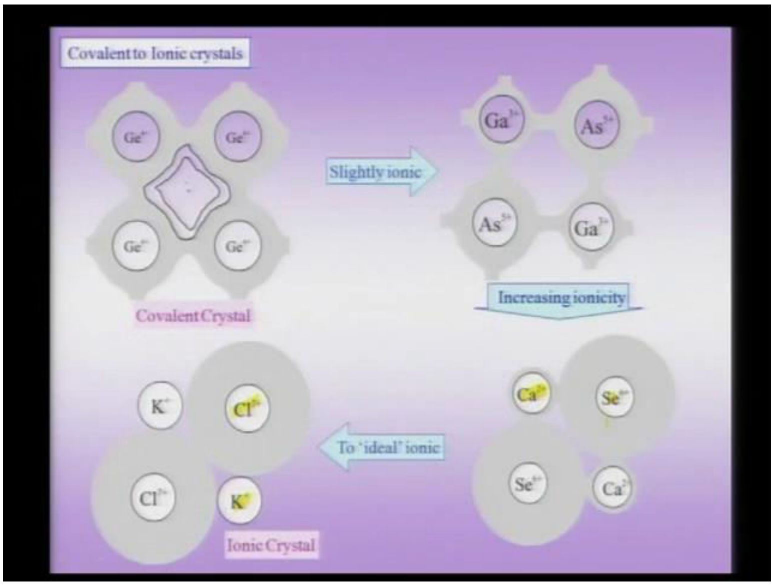

Covalent to Ionic crystals

So, next slide for instance we consider a progress for instance what you may call a nicely covalently bonded material to a case which is perhaps an ideally ionic material. So, in ideally covalent bonded material for instance we know germanium crystal which is crystallized in a diamond cubic structure. So, this is just a schematic please do not actually try to understand it in terms of the diamond cubic structure. This is just a schematic, so I should actually have replace this with a any n plus.

So, that should have been a better example, so you see this is a perfectly covalently bonded material, but if you take another case again this is being a schematic I am not actually trying to explain the actual structure. So, this is a gallium arsenide, so gallium 3 plus and arsenide arsenic 5 plus are the ions. And you can see that this has an ionic character, but this has a covalent character, but these 2 ions of being different there is a slight iconicity to this bond.

Even more, ionic kind of bond would be between calcium and selenium the calcium 2 plus and selenium 6 plus. So, you can see that these are the charges are there is a dispiriting the charges; that means, that the localization is not perfect. And there is a certain distribution of electron density in the; that means, there is a certain localization and there is also a certain de-localization. So, both are there here and therefore, this is somewhere between a perfect ionic bond and some between a perfect covalent bond.

Of course, you can have a perfect ionic crystal like which is the K C l crystal and which the K plus and C l 7 plus. They are the 2 ions and you can see that the electrons have been highly localized in this case. So, in this is perhaps a nice schematic slide though we should not read into the exact structure or even perhaps the exact electron density because as you know this perhaps this surface here. What is actual line might represent would be a certain electron density. So, this configuration which you see here is outlined actually perhaps represents a certain electron density.

So, this would for instance suppose this represented say 0.05 electron volt, then there would be a contour which would go inside this which would have a even lower electron density. It does not mean that it straight abruptly goes to 0 here. So, there is a distribution of electron density progressively going to 0 somewhere perhaps in the region which is at the centre. So, we have to be little careful in interpreting these diagrams, but the overall message which is sort of the purpose of this slide is the understanding.

That you can have purely covalent bonding, you can have a slightly ionic nature to this covalent bonding. You can have bonding which is somewhere in between an ionic and covalent bonding. And finding you can have a bonding which is purely ionic kind of a bonding. So, these all these possibilities exist and therefore, the structure we have seen special example we saw that we what you call we use a Pauling's rules or the rules for the understanding the formation of ionic crystals.

And we said when we took up this structure of zinc blende we could no longer rationalize that kind of a bonding based on the rules of the ionic crystal. So, we have to go to more covalent character therefore, it had to be the kind of bonding was a tetrahedral kind of bonding.

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COVALENT SOLIDS (CRYSTALS)

So, now, we are in a position to take up covalent crystals having understood that there are of course, these perfect covalent crystals, but there are other crystals which have certain iconicity to the bonding.

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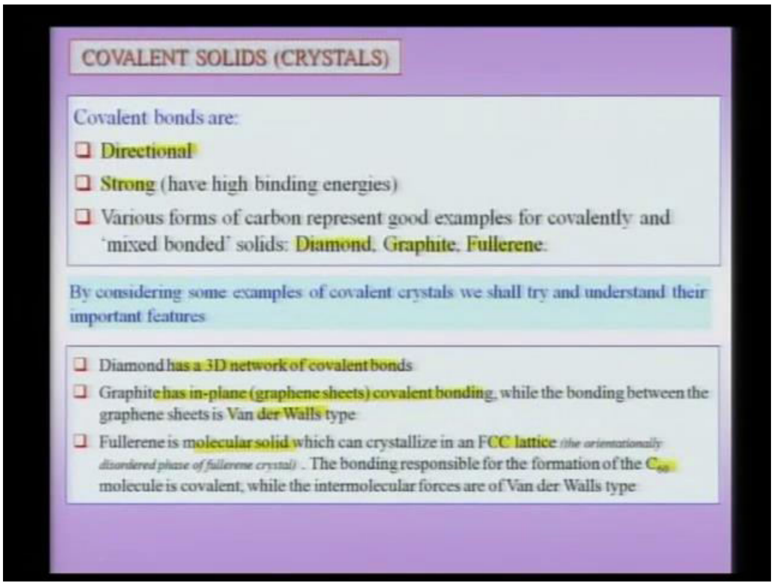

COVALENT SOLIDS (CRYSTALS)

Covalent bonds are:

- ☐ Directional
- ☐ Strong (have high binding energies)
- ☐ Various forms of carbon represent good examples for covalently and 'mixed bonded' solids: Diamond, Graphite, Fullerene.

By considering some examples of covalent crystals we shall try and understand their important features

- ☐ Diamond has a 3D network of covalent bonds
- ☐ Graphite has in-plane (graphene sheets) covalent bonding, while the bonding between the graphene sheets is Van der Walls type
- ☐ Fullerene is molecular solid which can crystallize in an FCC lattice *(the orientationally disordered phase of fullerene crystal)*. The bonding responsible for the formation of the C_{60} molecule is covalent, while the intermolecular forces are of Van der Walls type

So, the of course, we already know the characteristics of a perfect sort of a covalent bonding. The covalent bond is highly directional and they are very strong. typically, they have very high binding energies and the various forms of carbon which we will take up examples, and some of them we have already considered are perhaps the best examples to understand covalent bonding.

Now, carbon needless to say is perhaps the most important element it is a source of all life, but with regard to even formation of crystal structures. You can note that it is role is very, very important, not to say even as an alloying element in steel which we perhaps we will see later in the course. That it can give lot of hardness to ion and the steel is a very hot form especially, when it forms a phase called the martensitic phase.

So, carbon is very, very important then the important ion tropic forms of carbon. We know are diamond, we know graphite and we will consider fullerene today's lecture. There are other forms of carbon which are also lot of important to research from the single sheets of which you isolate from graphite which are called graphing sheets is a topic of intense research now. There are nano tubes of carbon which are also topic of hot research and therefore, there are carbon is although more in lot of focus and attention in academy at now-a-days.

For instance when you have diamond, diamond has a 3 D network of covalent crystals. covalent bonds graphite has in-plane covalent bonding while the bonding between the sheets is a Van der Walls type. So, you can see already when you go from diamond to graphite the bonding character changes and this also changes it is properties. For instance diamond is a nearly a perfect insulator, electrical insulator. Though, it is a good thermal conductor it is an electrical insulator.

While graphite is a good electrical conductor and this is coming from the high orbital's which exists and which can conduct electrons. The other example which I told you fullerene which we shall take up in considerable detail today is a molecular solid. So, this is an example of a molecular solid and this has not to be confused with the other cases of solids like the covalent crystals. So, even though in the topic of covalent crystals we will take up an example of a molecule solid within this because it is a beautiful example made of carbon.

And we will see that typically it can have an F C C crystal structure or a simple cubic crystal structure depending on. If it is the orientationally ordered state or the orientitionally disorder state, so we will take up C 60 also in detail even though it is not a an example of a covalent crystal. So, please remember once again as a warning that even though we are talking about covalent crystals, we are taking up this additional example of fullerene to understand the case of molecular crystals. And this one example of fullerene will throw into light many other important concepts, some of which of course, will be a revision of what you already studied before.

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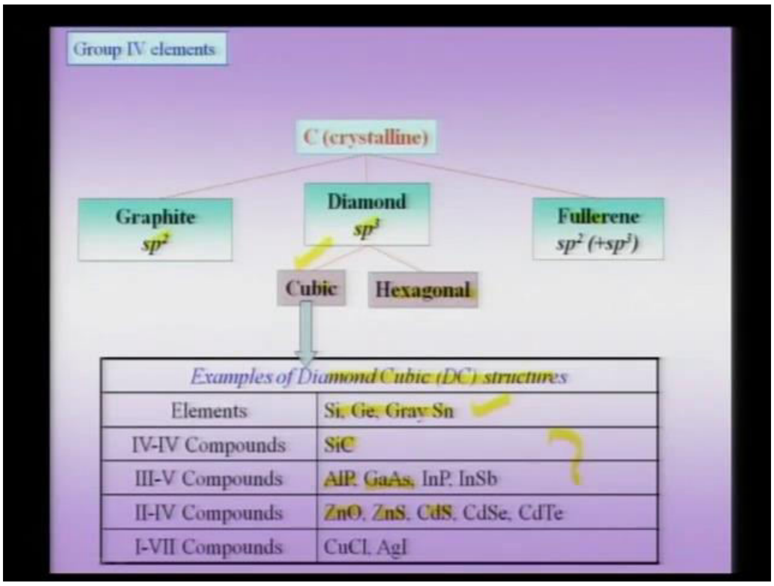

Group IV elements

C (crystalline)

Graphite
sp^2

Diamond
sp^3

Fullerene
$sp^2 (+sp^3)$

Cubic

Hexagonal

Examples of Diamond Cubic (DC) structures	
Elements	Si, Ge, Gray Sn
IV-IV Compounds	SiC
III-V Compounds	AlP, GaAs, InP, InSb
II-IV Compounds	ZnO, ZnS, CdS, CdSe, CdTe
I-VII Compounds	CuCl, AgI

So, if you look at the crystalline forms of carbon I said graphite which is s p 2 hybridized diamond which is s p 3 hybridized. And diamond of course, there are 2 forms of diamond the cubic and hexagonal form. So, we will basically focus on the cubic form and of course, you already done, so in considerable detail before. So, today is will be just your revision of the previous considerations and of course, additional 1 which is fullerene. And the important note that fullerene does not have pure s p 2 or pure s p 3 hybridization.

So, that is because now if you flat graphing sheet that would be s p 2 hybridized while, this is a case of a graphing sheet being which is bent and therefore, the hybridization is not purely s p 2. So, examples of diamond cubic crystal structures many approach we already seen like the silicon, germanium and gray tin. There are compounds important compounds in silicon carbide which is a very hard phase and which has important technological application.

We have seen the semiconductor examples like aluminium phosphate, gallium arsenide and indium phosphate and there are oxides also like zinc oxide, zinc sulphide and cadmium sulphide which are also very important technologically. So, there are many examples of structures which go into; that means, elements and also compounds which are all these are all compounds which go into the diamond cubic structure

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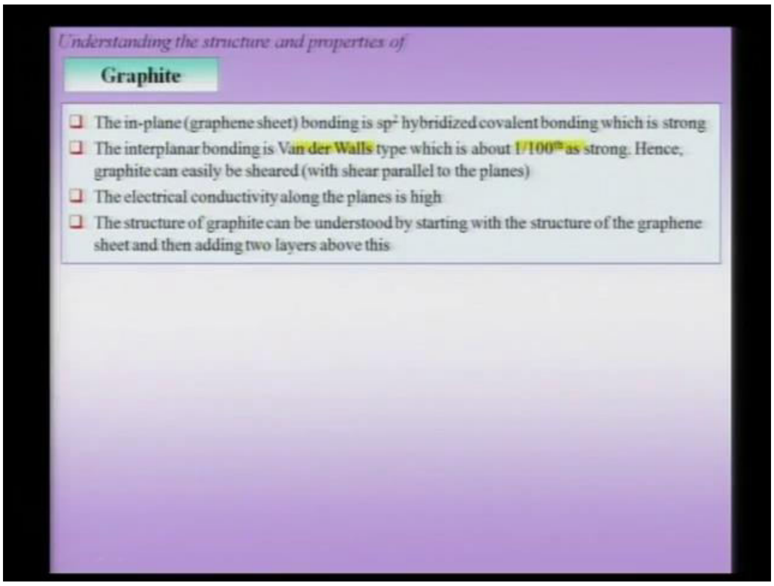

Understanding the structure and properties of

Graphite

- ☐ The in-plane (graphene sheet) bonding is sp^2 hybridized covalent bonding which is strong
- ☐ The interplanar bonding is Van der Walls type which is about 1/100th as strong. Hence, graphite can easily be sheared (with shear parallel to the planes)
- ☐ The electrical conductivity along the planes is high
- ☐ The structure of graphite can be understood by starting with the structure of the graphene sheet and then adding two layers above this

Since, we have already done taken up the case of graphite in detail before the structure of graphite perhaps this is just be a small brief revision. I will go through this topic very fast including the case of the diamond, but never the less these are important structures to consider. So, we have noticed that the properties of graphite are strongly dictated by the kind of bonding the in-plane covalent and the out of plane or between the graphing sheets the Van der Walls type of bonding. And we had seen that it is about 1000^{th} as strong 100 as strong as the covalent bond and the in-plane electrical conductivity is high because of the kind of bonding.

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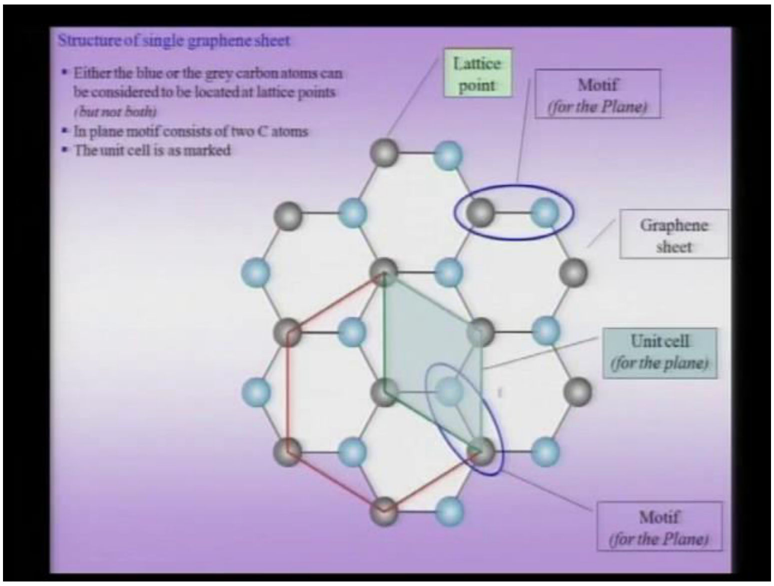

Structure of single graphene sheet

- Either the blue or the grey carbon atoms can be considered to be located at lattice points *(but not both)*
- In plane motif consists of two C atoms
- The unit cell is as marked

So, we had seen that first we need to understand the structure of graphite, we need to understand the in-plane structure and we already drawn for instance this was the unit cell of the in-plane structure. So, this is my in-plane unit cell and we had considered this in terms of the language of the lattice and the motif.

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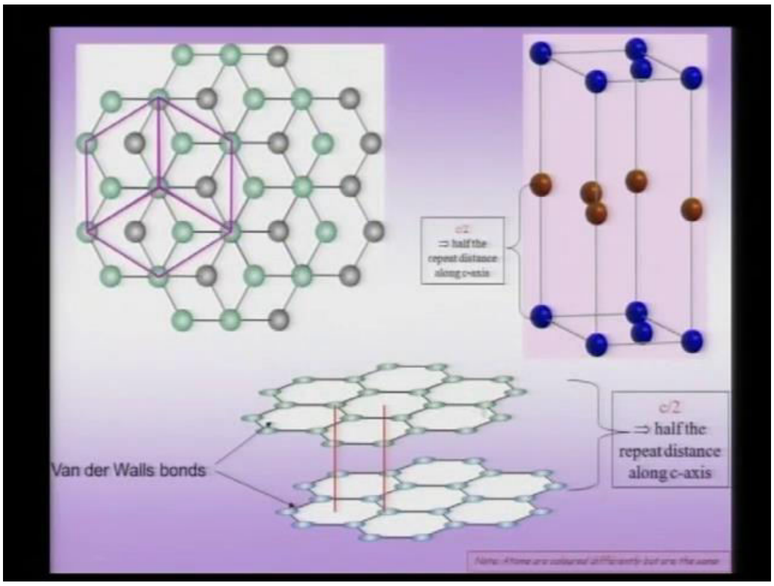

Then we went on to draw the 3 dimensional structure of this graphite in which we had noticed that we have to actually stag. The planes, which has staggered with respect to each other and you get half the repeat distance which is shown here in the green and the blue coloured planes.

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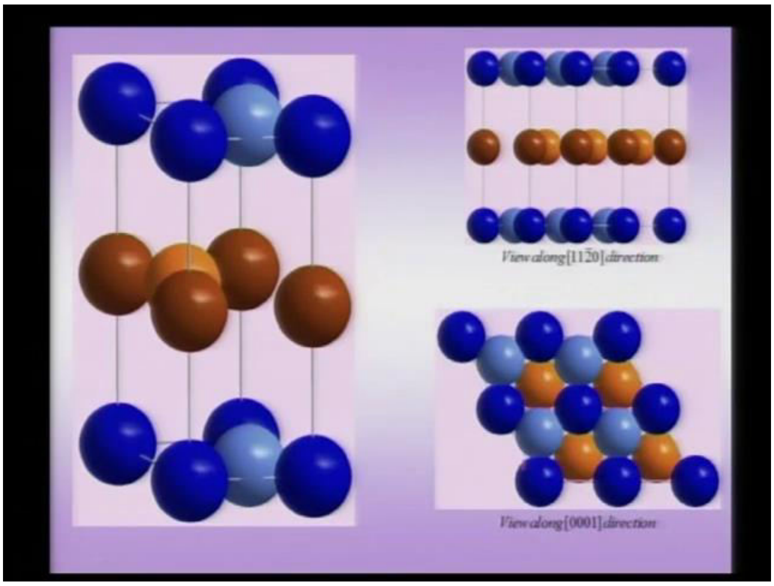

So, this all this we had already seen, so I am just grossing over this topic for understanding of the graphite structure.

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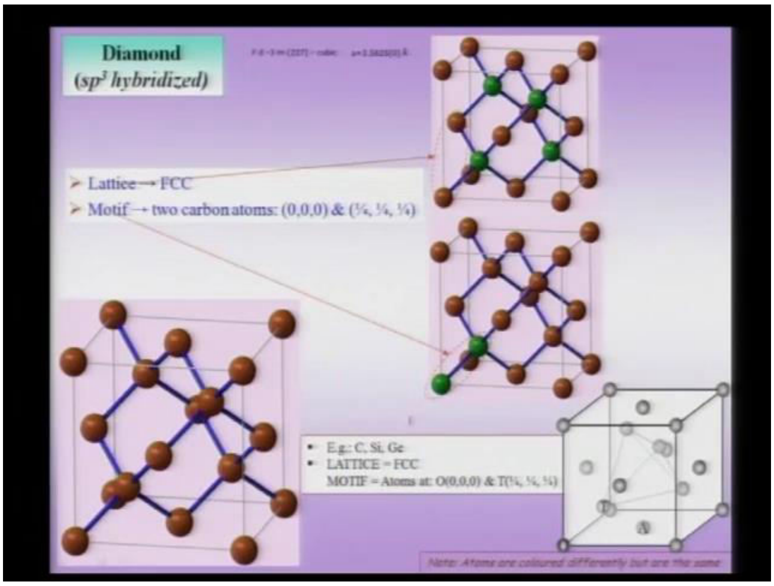

Diamond
(sp³ hybridized)

- Lattice → FCC
- Motif → two carbon atoms: (0,0,0) & (¼, ¼, ¼)

- E.g.: C, Si, Ge
- LATTICE = FCC
  MOTIF = Atoms at: O(0,0,0) & T(¼, ¼, ¼)

Note: Atoms are coloured differently but are the same

Similarly, we had also seen diamond in detail we had noticed that is called an F C C lattice and there is a 2 carbon atom motif which actually decorates this lattice.

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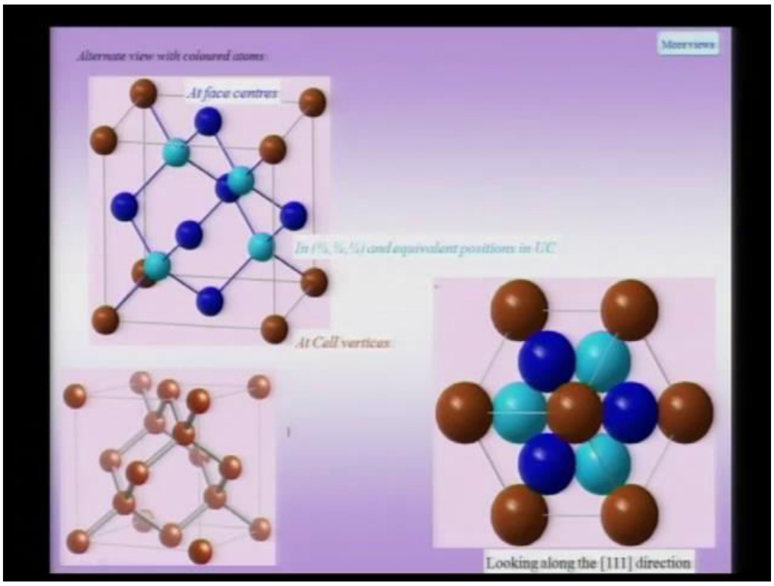

Alternate view with coloured atoms

More views

At face centres

In (¾,¾,¾) and equivalent positions in UC

At Cell vertices

Looking along the [111] direction

And we had also notice that for instance if you look at the diamond cubic structure the tetrahedral bond actually pervades. And we had sited this is an example wherein there are no close packed direction, no close packed planes and the structure itself was not a close packed structure.

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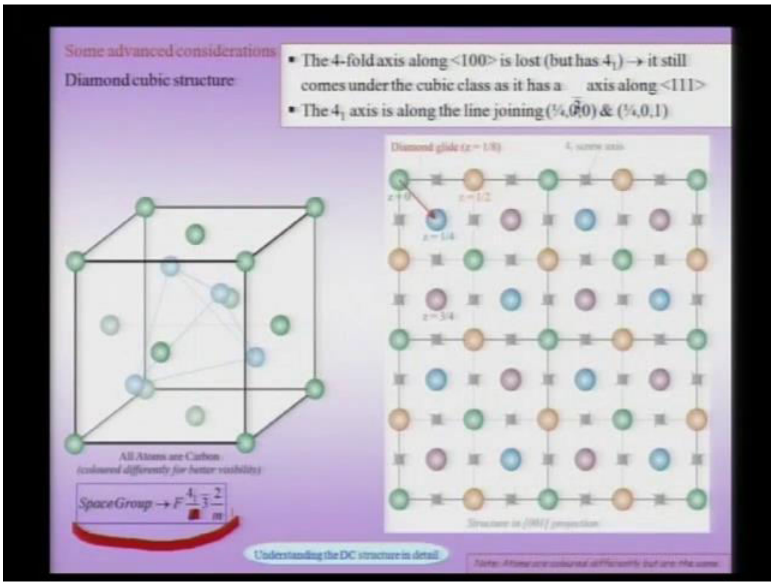

Some advanced considerations

Diamond cubic structure

- The 4-fold axis along <100> is lost (but has 4_1) → it still comes under the cubic class as it has a axis along <111>
- The 4_1 axis is along the line joining (¼,0,0) & (¼,0,1)

All Atoms are Carbon (coloured differently for better visibility)

Space Group → $F\frac{4_1}{\blacksquare}\bar{3}\frac{2}{m}$

Structure in [001] projection

Understanding the DC structure in detail

Note: Atoms are coloured differently but are the same

Additional thing we try to understand using for the structure is a fact that actually the concept of what is known as the diamond glide which is present in the structures. The d which is present as you can see in the space group which is drawn below. So, you can see that there is the diamond glide and also we try to understand that why this is called a cubic structure. Even though it has no 4 fold axis and what is the kind of axis which is really got and we note that it actually had a 4 1 screw axis. So, this part we had noted before.

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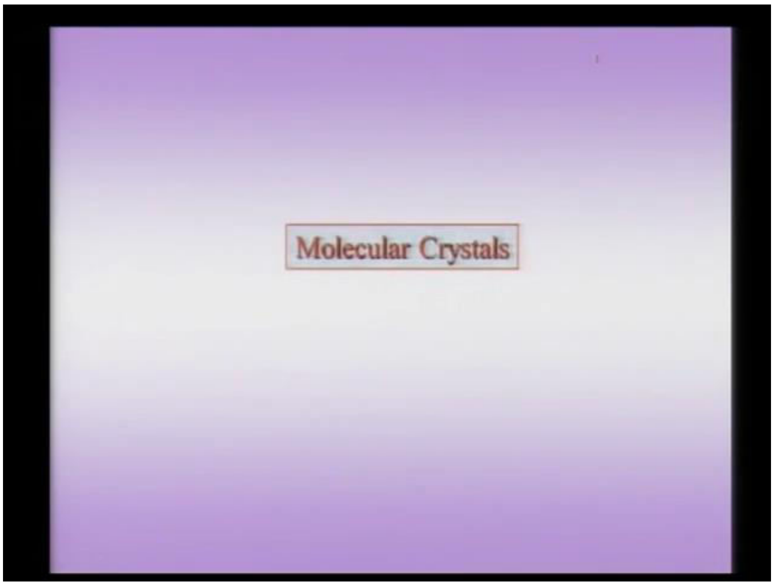

Molecular Crystals

So, this is perhaps the right time to also consider this molecular crystals and we will consider the example of fullerene.

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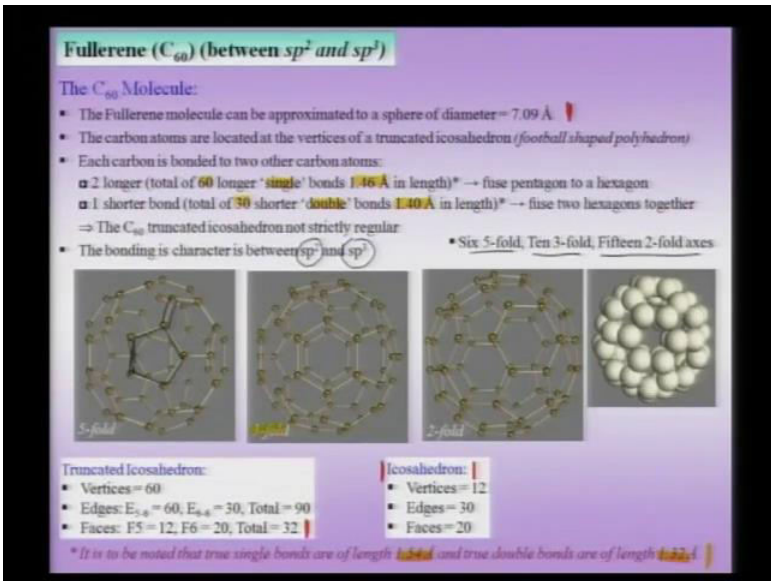

Fullerene (C_{60}) (between *sp^2 and sp^3*)

The C_{60} Molecule:

- The Fullerene molecule can be approximated to a sphere of diameter = 7.09 Å
- The carbon atoms are located at the vertices of a truncated icosahedron *(football shaped polyhedron)*
- Each carbon is bonded to two other carbon atoms:
  - 2 longer (total of 60 longer 'single' bonds 1.46 Å in length)* → fuse pentagon to a hexagon
  - 1 shorter bond (total of 30 shorter 'double' bonds 1.40 Å in length)* → fuse two hexagons together

  ⇒ The C_{60} truncated icosahedron not strictly regular
- The bonding is character is between sp^2 and sp^3

- Six 5-fold, Ten 3-fold, Fifteen 2-fold axes

Truncated Icosahedron:
- Vertices = 60
- Edges: $E_{5-6} = 60$, $E_{6-6} = 30$, Total = 90
- Faces: F5 = 12, F6 = 20, Total = 32

Icosahedron:
- Vertices = 12
- Edges = 30
- Faces = 20

** It is to be noted that true single bonds are of length [illegible] and true double bonds are of length [illegible]*

So, what are molecular crystals when we classified crystals, we said there are 2 type of crystals. One are molecule crystals and other are non-molecular crystals, in non-molecular crystals we had seen the metallic ionic and covalent crystals. We said molecule crystals are those crystals wherein the bonding within the molecule is typically covalent, but the forces or the bonding which is giving rise to the formation of the crystal is typically of a weak type which could be Van der Walls or some other kind of weak interaction and one of the other interactions possible is hydrogen bonding.

So, common examples of for instance a molecular crystal would be the ice crystal. In ice crystal there is covalent bonding between the oxygen and the hydrogen atoms, but the forces giving rise to the formation of the crystal is the hydrogen type of bonding which is and you know, this is a very special kind of bonding wherein actually ice expands on freezing which is very, very important. As you know because if ice actually contracted on it would be heavier than water.

It would sink and perhaps all the oceans would freeze up while, because ice actually floats on freezing, actually itself provides the insulating layer. And the remaining water remains not frozen which is important from the point of view of life. So, the other example of an important ion molecular crystal is this fullerene, the fullerene has to if we want to understand the fullerene crystal structure we should start with the C 60 molecule.

So, let me show you a example of a model for instance of a C 60 molecule. So, I have here model of this C 60 molecule, to understand this structure of the C 60 molecule which is very similar to the structure of a football. I can start with an icosahedron and you know as from before the icosahedron has 5 fold axis 3 fold axis and 2 fold axis. So, if you connect the opposite 2 edges you get a 2 fold axis and there are 3 orthogonal 2 fold axis.

For instance this would be a 2 fold axis the 1 vertical would be a 2 fold axis and the third orthogonal axis can also be a 2 fold axis. Now if I start with an icosahedron and then truncate my vertices, I truncate all the vertices. Then each 1 of these vertices will become a pentagon, these originally triangular faces will become hexagons therefore, now you will have pentagons surrounded by hexagons. That means, no 2 pentagons will touch each other actually the all the pentagon’s will be isolated and you will have hexagons around it and that is a structure we are seeing here.

So, in terms of the rotational symmetries an icosahedron is identical to the fullerene molecule which is a truncated icosahedron. So, this geometrical solid you can see again has this 3 fold axis which pass through the top and there are these pentagon's which are seeds of the 5 fold axis and of course, you have the 2 fold which are the vertices edges. Now, it is important to note that these pentagon's are isolated from these hexagons and as we shall see very soon that the kind of bond which is present between a hexagon and a pentagon.

This kind of a carbon-carbon bond, so carbons are present in all these vertices in a fullerene molecule, therefore, this is called a C 60. There are 60 of these atoms in this and you could not have higher analogues of C 60 like C 70 etcetera, but we will consider the simplest 1which is C 60 or the most common 1. So, you can see that carbon atoms are present in all the vertices. So, the kind of bonding between carbon-carbon which is here is different from the kind of bonding carbon-carbon which is between a pentagon and hexagon.

In other words if you consider a hexagon then you have carbon-carbon bonds which are shared between a pentagon and hexagon and there are carbon-carbon bonds which are shared between a hexagon and hexagon. These 2 carbon bonds are different and as we shall see from this slide. So, let us start by considering the icosahedron which is shown in the bottom lower part of the slide.

So, we talk about an icosahedron as here, you can see that an icosahedron has 12 vertices 30 edges and 20 faces. And this form as the follows the famous Euler's rule for convex polyhedral. So, this you can see that when I cut these 12 vertices therefore, I will get 12 more of these faces which form, so apart from the original phases. So, I will get my here total 32 faces which is what you see in the case of the truncated icosahedrons. The edges as I pointed out are of 2 kinds here unlike the icosahedrons, which are a single kind of edges.

So, in an icosahedron all edges are identical right and that is important to note why in the case of the truncated icosahedron we have 2 kinds of edges and this has to be noted. The edges which lie between hexagon and hexagon the edges lie between pentagon and hexagon. So, the edges can be of 2 types the E 5-6 edges between the pentagon and the hexagon, there are 60 in number.

The E 6-6 has the 30 in number there are total 90 edges. The vertices have to be 60 because that is why we put 60 carbon atoms along the vertices and I get a C 60 molecule. The faces again; obviously, of 2 types the pentagonal faces are 12 in number and the hexagonal faces are 20 in number. So, this also illustrates a principle that when you have pure hexagons tessellating space. Then you can only illustrate Euclidean flat space; that means, 2 dimensional Euclidean space and whenever I have to introduce curvature into space.

Then I need to introduce pentagons, which is also very clear from looking at this molecule. So, this fullerene molecule is in other words the single example from which we can understand many, many, many concepts and one of the concepts we will start by understanding is of course, the structure, the geometry, the symmetry and the concept of convex polyhedra and the concept of truncation. Then we will also try to understand the concept of orientational order disorder, we are also trying to understand the concept of a molecular solid.

That means we have the, it is a Van der zwan's bond which is lying to a giving rise to the formation of a crystal. So, there are many, many concepts we can understand by considering a single molecular crystal which is the fullerene crystal. Now these the fullerene molecule can be approximated to a sphere of diameter 7.09 angstrom and why this approximate needs to be done we will see when we actually talk about the fullerene crystal.

So, that will become obvious that why we need to approximate this why and or under what circumstances this can be approximated to a sort of a sphere. Now, as I said that carbon is bonded to other carbon by 2 kinds of bonds, casually sometime these bonds are called for instance the double bond and the single bond, but we looking at more carefully.

So, we will note that this actually not single and double bond. So, sometimes casually these are called single bonds and double bonds, but looking at the length of these bonds. We have to be little careful that these are not the true lengths which are normally formed for double bonds for instance single bonds are 1.54 angstroms in length carbon-carbon and double bonds are 1.32 angstroms.

But here, you will note that the longer bonds which are like the single bonds are 1.46 angstroms in length and the shorter bond is which is something like a double bond is 1.40 angstroms in length. So, though we might say the double bonds and single bonds what we mean is that these lengths are followed rather than the conventional lengths which are shown at the bottom. So, the longer bonds fuse pentagon to hexagon and the shorter bonds which are 30 in number.

So, the 30 shorter bonds and 60 longer bonds the 30 shorter bonds fuse to hexagons together right. So, let us I try to identify on the figures below with there are 3 figures of this fullerene molecule 1 with the 5 fold coming out of the plane of the slide. There is a 3 fold coming out of the slain of the slide and also there is a 2 fold coming out of the plane of the slide.

And of course, there is a model with hard sphere carbon atoms wherein you can also identify the 3 fold direction, so where are the double bonds and the single bond in this picture. So, the shorter bond is the double bond fuse to hexagons together. So, if when I am talking about a hexagon-hexagon bond, so this is my double bond. And the single bond sorry the wrongly because there is now choosing a pentagon to hexagon, so this is a single bond this is single bond and this is a single bond and this is single bond and a single bond.

So, the pentagon is formed by single bonds, but when I am talking about hexagon-hexagon that is a double bond, so this is my double. So, I have single bonds and double bonds in this structure and that is why this structure is not a regular truncated icosahedron because the bond lengths are different the edge lengths are different. So, this is a slightly different truncation it is not the truncation wherein you would obtain if I did a truncation.

Of course, I could do various kinds of truncation of this icosahedron for instance if I truncate a little bit then I will get very small pentagons and large hexagons which are not regular hexagons right. So, this is that kind of a structure where I have the truncation is not exactly in a way for instance I truncate little more. Such, that this edge which is formed by the truncation to the original remaining edge or both equal that would be a regular truncated icosahedrons, but the truncation in this case has been done in a way.

Such that, now my truncated icosahedron is not a regular truncated icosahedron and the 2 edge lengths are different. And; that means, that I have double bonds and single bonds decorating this C 60 fullerene molecule. So, we have to remember now, so far we have not considered the crystal we just dealing with the molecule. And as I pointed out in this case the bonding character is somewhere between s p 2 and s p 3. If you had simple graphing sheets the bonding character would be a s p 2 hybridization, but now you are bending these graphing sheets. And therefore, the bonding character is changing and it is not purely an s p 2 hybridized molecule.

So, the total number of rotational axis you can see there are 6 5 fold, 10 3 fold and 15 2 fold axis and you will see the various perspectives along the 3 important symmetry directions of the fullerene molecule. So, to revise the fullerene molecule before we proceed to the fullerene crystal, the fullerene molecule is a completely a separate form of carbon. And perhaps fullerene nano tubes etcetera are the some of the important exciting examples of other forms of carbon apart from diamond and graphite.

In some sense fullerene molecule can be considered as a sort of a buckled form of the graphite, graphing sheet though, but you can see clearly that to do. So, you need to introduce pentagons and you cannot have a structure with purely hexagons. And in many of the what you call understanding crystal structure we can approximate this to be like a really like a football in other words like a sphere of watts 7.09 angstrom in length. So, we will start with this fullerene molecule and try to understand the formation of the fullerene crystal.

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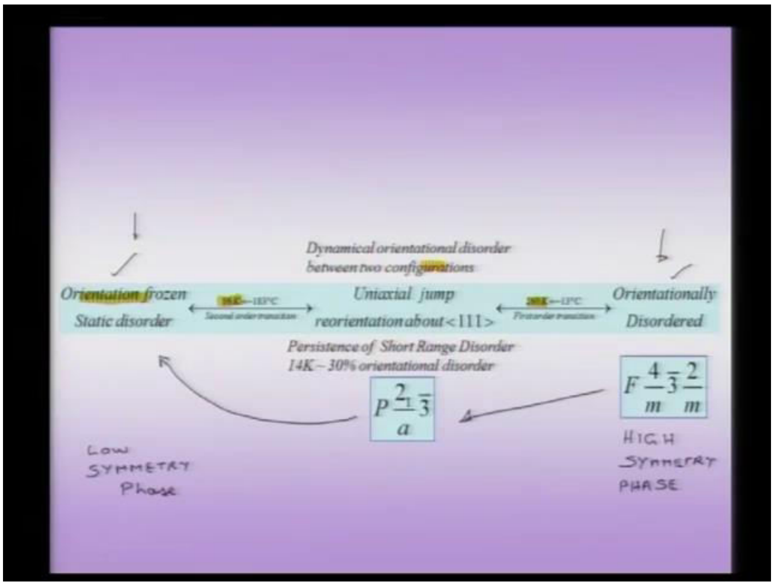

Dynamical orientational disorder
between two configurations

Orientation frozen
Static disorder

90K – 183°C
Second order transition

Uniaxial jump
reorientation about <111>

260K – 13°C
First order transition

Orientationally
Disordered

Persistence of Short Range Disorder
14K – 30% orientational disorder

$P\frac{2_1}{a}\bar{3}$

$F\frac{4}{m}\bar{3}\frac{2}{m}$

LOW
SYMMETRY
Phase

HIGH
SYMMETRY
PHASE

So, if you consider the various crystalline forms of fullerene. We can identify basically 3 regions with respect to temperature, the high temperature which is of course, including room temperature is the temperature region higher than 260 Kelvin. You can see that the structure of fullerene crystal is a orientationaly disordered form of fullerene which has a symmetry of f 4 by m 3 bar 2 by m crystal. So, it is nothing but an normal F C C crystal.

So, instead of having a motif which would be a say a copper ion or a aluminium ion here now you have an entire molecule which is an motif, and therefore and if what is sitting on the conventional lattice positions of the F C C lattice. There are no atoms in fact it is a centroid of this fullerene molecule which is occupying the position of the lattice point. In other words as I pointed out before this will be a nice example also of case wherein there are no atoms sitting on lattice points, but each lattice point is associated with a fullerene molecule.

So, that is the one of the concepts also clarify, so what do I mean by this orientationally disordered face we will see soon, but before that we will complete the other kind of faces which the systems forms. If you look at the temperature region between 260 Kelvin and about 90 Kelvin, you actually find a partially ordered, partially orientationally ordered kind of a fullerene structure wherein the structure of the fullerene molecule jumps or between 2 orientations.

There is still partial orientational disordered and therefore, this is still not an fully ordered crystal. And of course, the parts where there is actually this should be drawn here, the fully orientationally ordered crystal is the one which has actually the p 2 by one by a 3 bar. Symmetry, in other words, so let me draw this here, so this actually belongs to the full ordered state, orientationally ordered state. And this crystal; that means, lowers it is symmetry from the high symmetry, so this is my high symmetry region this is high symmetry phase.

And this is the low temperature phase which is below 86 Kelvin and this is the low symmetry phase. The high symmetry phase is the orientationally disordered phase and the low temperature phase is the orientationally frozen phase or it is a orientationally ordered phase. We had considered one example of an orientationally ordered structure, but this is perhaps even more interesting example of an orientational ordered disordered transformation. So, let us look at these 2 structures specifically and the 1 which is the high temperature 1 here and the low temperature 1 which is here which is the orientationally ordered structure.

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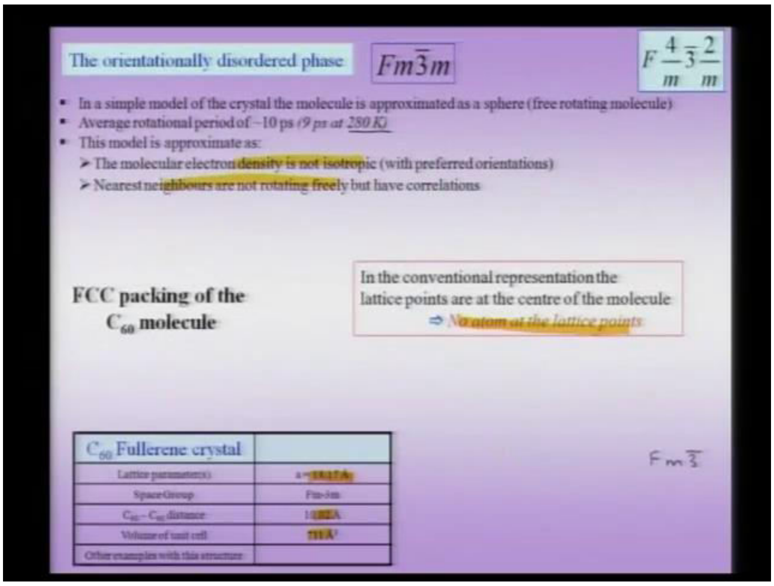

The orientationally disordered phase

$Fm\bar{3}m$

$F\frac{4}{m}\bar{3}\frac{2}{m}$

- In a simple model of the crystal the molecule is approximated as a sphere (free rotating molecule)
- Average rotational period of ~10 ps *(9 ps at 280 K)*
- This model is approximate as:
  - ➢ The molecular electron density is not isotropic (with preferred orientations)
  - ➢ Nearest neighbours are not rotating freely but have correlations

FCC packing of the C_{60} molecule

In the conventional representation the lattice points are at the centre of the molecule

⇒ *No atom at the lattice points*

C_{60} Fullerene crystal	
Lattice parameter(s)	a = [illegible]
Space Group	Fm-3m
C_{60} – C_{60} distance	[illegible] Å
Volume of unit cell	[illegible] $Å^3$
Other examples with this structure	

$Fm\bar{3}$

So, let me first try to understand the orientationally disordered phase which is got the symmetry of the perfect or the cubic lattice itself which is 4 by m 3 bar 2 by m. Now, in this case why can we now approximated to a sphere because if we are putting anything of lower symmetry than a sphere. Of course, now I will be known from our knowledge of crystallography that I need to look at not only the motif decorating the lattice point, but also the orientational motif decorative lattice point.

And clearly this has symmetry which is not consistent with the cubic lattice; that means, the symmetry of the structure if you put this for instance fullerene molecule say for instance the 2 fold upwards identically at every lattice point. Even in that case you would actually get not the f 4 by m 3 bar 2 by m symmetry, but you will get a space group which is F I think 4 C or one of those symmetries you will get a F 3 bar.

The second place has to be a 3 bar, so it will be a symmetry of that structure will be f I think m 3 bar. So, I think this is will be the symmetry of the space group with which you will obtain the structure. In other words even if you put a sphere of fullerene identically every lattice point you will not get the higher symmetry possible for the F C C lattice, but now suppose I now ignore the orientation symmetry and how can I do it.

You can do it because if you notice that fullerene molecule at room temperature for instance example given here a 280 Kelvin for instance. We notice that the molecule is rotating and the average rotational period is of the order of ten picoseconds. So, the molecule is consistently rotating, and therefore we can approximate this molecule to be sphere; that means, this orientational disordered phase what I mean is that this molecule is rotating, and therefore because of the continuous rotation as molecule with about a period of ten picoseconds.

I can assume that this is a sphere and therefore, I can assume that spheres are decorating the lattice points in an F C C lattice. And therefore, I can now the orientational disordered phase in other words I am actually if I of course, I freeze my time picture I would get a certain orientation of all of these truncated or the fullerene molecules. Now, that as you can see would be perhaps a glass a true description of that would be a glass, but now if I had ignored the orientation symmetry or otherwise considered this spherical orientational symmetry I consider this a sphere.

Then this crystal would have this kind of a high symmetry and this is nothing but the orientational disordered phase of F C C crystal of the fullerene molecule. Of course, even this orientational complete approximation of a sphere is an approximation in reality you will note that the molecular electron density is not isotropic. That means, there are some preferred orientations to this electron density and additional complications arising that the nearest neighbours are not rotating freely, but they have some correlations.

So, even this model of freely rotating sphere which is totally uncorrelated with it is neighbours is an approximation, but that is a good approximation in more circumstances. And we can assume this crystal to be having a symmetry F 4 by m 3 bar 2 by m which means it is an F C C crystal. And added to this you can notice that apart from the pointed I noted out that no atoms actually sitting on the lattice point.

This is when extreme example or a very good example of case wherein you have an F C C crystal, but it is actually nowhere near close packed. Of course, if I consider this as a hard sphere yes these hard spheres are close pack, but if we took at the packing fraction in terms as the volume occupied by the carbon atoms, then this will have a extremely low packing fraction.

So, depending on the definition of the packing fraction and of course, I am using a definition now that the carbon volume occupied by the carbon atoms with respect to total volume available in the crystal. Then this would be a very poor packing of atoms in space, in other words even though this is a F C C crystal this is definitely not a close packed crystal.

So, this is a for the emphasizing some of the points we already considered doing our earlier lectures. The lattice parameter of the this crystal is 14.179 angstrom which is a large lattice parameter the space group we already seen the carbon C 60 is distance about 10 angstroms. The centre to centre distance that is and the volume of the unit cell is pretty large is about 711 angstrom cube, so this is the orientationally disordered structure of fullerene.

So, we saw that when the orientations of the frozen in and now this is not randomly frozen in orientation, but very specific orientations into which it get an frozen and orientationally ordered phase actually as a lower symmetry. That means, the symmetry is lower when you have orientational ordered which we already seen before. The disordered phase typically is of the higher symmetry and the ordered phase is a lower symmetry and this is an example with respect to orientational order and not with respect to positional ordered.

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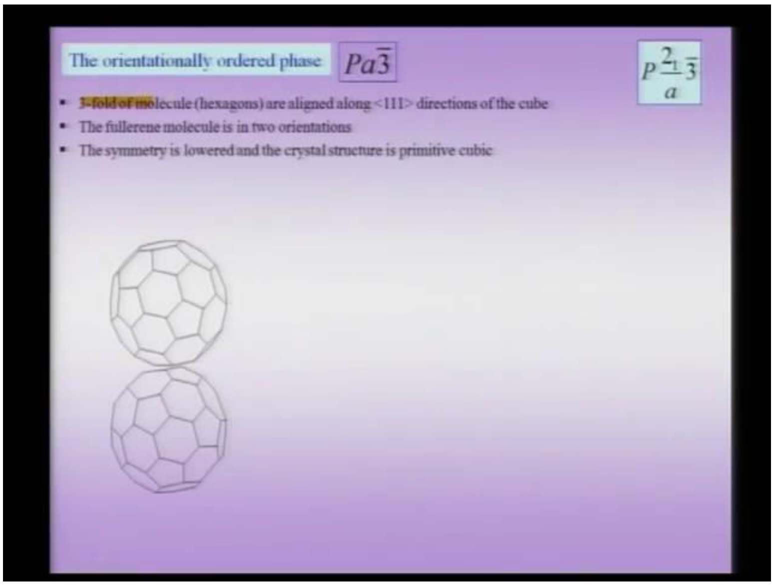

The orientationally ordered phase $Pa\bar{3}$

$P\frac{2_1}{a}\bar{3}$

- 3-fold of molecule (hexagons) are aligned along <111> directions of the cube
- The fullerene molecule is in two orientations
- The symmetry is lowered and the crystal structure is primitive cubic

Now, so to have it still call it a cubic crystal we need to have these 3 or 3 fold 3 or 3 bar axis and this is still the original 3 fold axis of the molecule which is the fullerene molecule..

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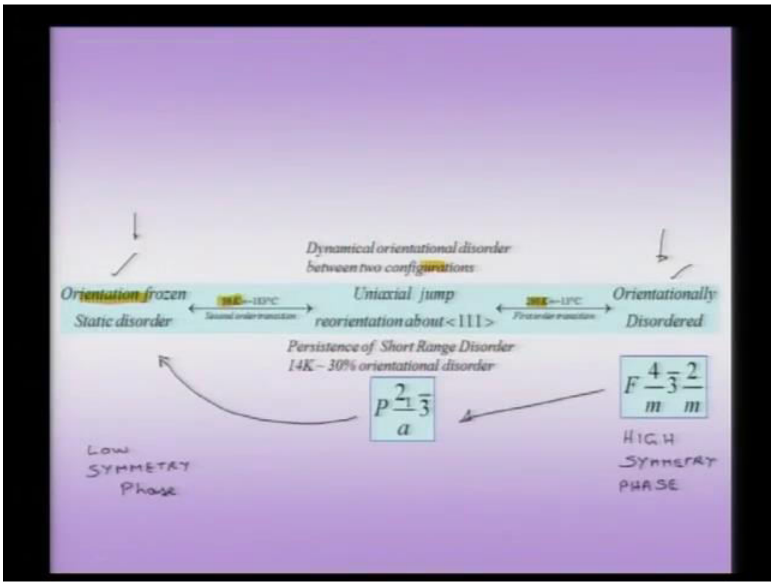

Dynamical orientational disorder between two configurations

Orientation frozen Static disorder

[illegible] ~-183°C Second order transition

Uniaxial jump reorientation about <111>

[illegible] ~-13°C First order transition

Orientationally Disordered

Persistence of Short Range Disorder
14K ~ 30% orientational disorder

$P\frac{2_1}{a}\bar{3}$

$F\frac{4}{m}\bar{3}\frac{2}{m}$

LOW SYMMETRY Phase

HIGH SYMMETRY PHASE

The fullerene molecule of course, in the intermediate regions if you want to consider some of the details, actually there are 2 preferred orientations. And the and 1 of them is a energetically favourable and as you go to lower and lower temperature the preferred orientation energetically preferred orientations are freezes in more.

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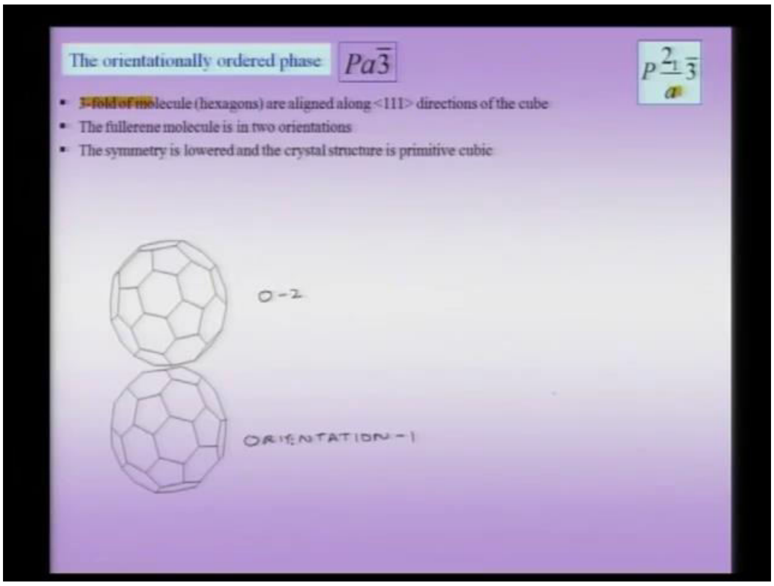

The orientationally ordered phase $Pa\bar{3}$

$P\frac{2_1}{a}\bar{3}$

- 3-fold of molecule (hexagons) are aligned along <111> directions of the cube
- The fullerene molecule is in two orientations
- The symmetry is lowered and the crystal structure is primitive cubic

And that preferred orientation would have for instance these 2 fullerene molecules in 2 different orientations, one orientation would be all the fullerene molecules located at the lattice point corners; that means, the cube corners. And the once which are located at the phase centres would have a different orientation, and actually these 2 positions are actually connected by a glide if you want to look at the details. Therefore, the fullerene molecule now as 2 orientations and; that means, no longer it is an F C C crystal it is actually primitive crystal.

And the fullerene molecule which is now located the phase centric position, go part of the motif and they are no longer lattice points. So, that point has to be noted and the symmetry of now this is structure has been lowered because this orientation ordered. And if you want to look at specifically at the order of the molecule itself, there are 2 orientations in to which the molecules are frozen in.

And we can understand these 2 orientations are those orientations which are located at the cube corners and the other orientations. For instance suppose I called this orientation 1, so this my orientation 1 and this is my orientation 2. So, we can see that let me draw this on board may be that is clear. So, I have my cube here.

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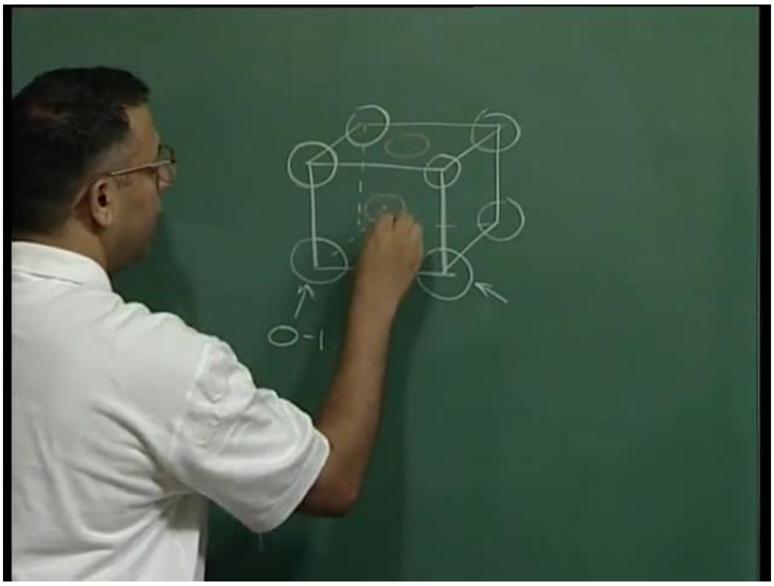

So, the fullerene molecule sitting in the cube corners, for these fullerene molecules come very close just for schematic I am drawing them little far away. So, these all will be in orientation 1 O 1 and the 1 which is sitting in phase centre which now, the phase centres are not lattice points anymore in the orientationally ordered state. And they would be orientation 2 and now this is my primitive cubic or a simple cubic crystal, now each lattice point having more than 1 fullerene molecule.

So, as we can see that fullerene is a very interesting example in many, many, many senses including in the formation of an F C C crystal, primitive cubic crystal. And also the vary structure of the fullerene molecule itself is very, very interesting to analyze in terms of the symmetry of the molecule starting with the icosahedrons. As, you know that the icosahedral symmetry is inconsistent with the formation of crystals and when we try to combine the symmetry of an icosahedrons symmetry with the cubic symmetry.

You can see that the symmetry of the structure is lower and actually you get 3 a 3 bar kind of a symmetry in the fullerene crystal. So, with this we come to a end of the sort of the consideration of ionic and covalent crystal. Next we are in a good position to start discussion about defects in crystals, but tell as a question before we proceed to defects in crystal.

Student: As my knowledge if crystal close packing I means packing fraction is very low. So, they form some they forms not too much hard crystal, but if we insert some C N T polymer matrix then so on practically it is a come too much harder.

Very important, very important question. So, you ware asking about 2 concepts and perhaps you should not confuse these 2 concepts, 1 concept is the concept of packing fraction, another concept is a concept of bonding. Now, suppose I consider a F C C crystal like copper which perhaps as a higher packing fraction a crystal like diamond like carbon diamond, but even though carbon as a diamond as a lower packing fraction it has much hardness. It is much more difficult to deform diamond and this is coming from this covalent kind of bonding.

Now, with respect to specifically when you are talking about crystals and packing fractions. Even though if I am the question you are asking is that now suppose I take a carbon nano tube or a fullerene molecule or a form of fullerene molecule crystal or put fullerene in a polymer matrix. What is the role they play and what is the role they play de-formation? As if the question we are asking and especially with regard to property like hardness.

Now, when you try to deform a fullerene crystal you are actually, trying to deform the not the carbon-carbon covalent bonding, but actually trying to deform the van der zwan's bonding that is what will get deform. Therefore, the crystals be very soft in fact, the lamellae melting point because of this reason. Now, when you putting it isolated molecules inside polymer matrix the when you trying to and assuming there is an isostrained condition; that means, fullerene molecules nicely bonded to the polymer abounded.

When you are trying to strain the polymeric matrix, then the carbon bond which you will try to strain in the fullerene molecule would be the covalent kind of bonding in which case it will actually show it good strength. Now, this is very similar to sharing of a graphing crystal suppose you try to share a graphing crystal along the planes. So, these are may now my graphing planes and I got graphite crystallize shear it in this case I am trying to deform my Van der zwan's bonds and it will actually show very low shear modulus. But, suppose now I pull along the planes; that means, now I have 2 options I have my graphing planes here.

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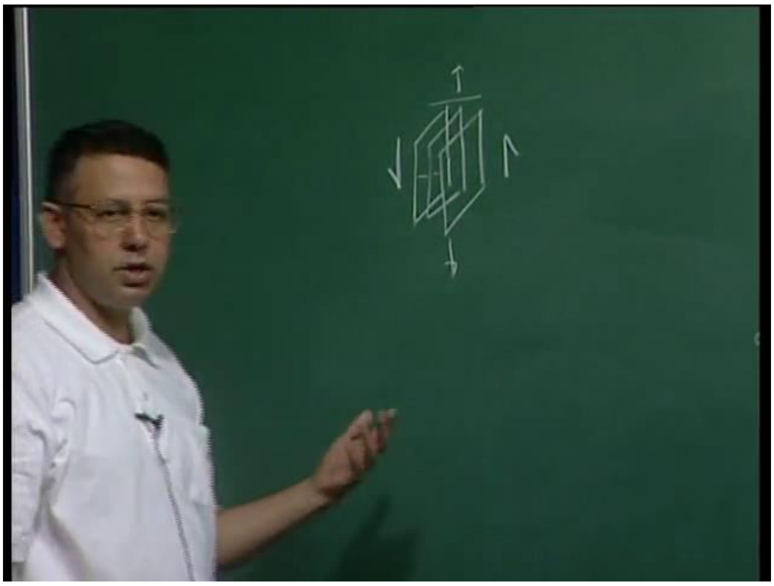

I am not drawing them excellence, but planes of graphing which form the crystal. So, now, suppose I am sharing my planes like this my shear is this direction. Then the van der zwan's bonds between the planes is going to be shared and this crystal is going to be extending weak. On other hands suppose I pull along these 2 planes the graphite planes then actually I will be stretching the carbon-carbon covalent bond in which case the crystal will be strong.

So, we have to clearly make sure that along with packing fraction, now the reason for the packing fraction. If we look at the macroscopic scale, there the definition of packing fraction is more light like porosity or what you might call the density of the material. We as compared to the theoretical density right, in that case you keep on doing more and more of material from the thing which is now macroscopic picture. In that case; obviously, modulus is going to come down. And that picture has not to be confused the microscopic picture, when I am talking about bonding and the kind of bonding you have distorting while actually getting a property.

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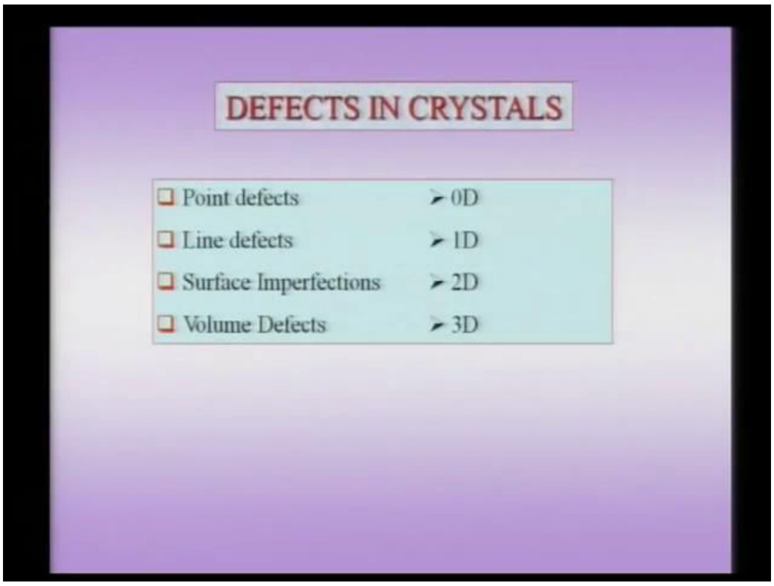

DEFECTS IN CRYSTALS

- ❑ Point defects ➢ 0D
- ❑ Line defects ➢ 1D
- ❑ Surface Imperfections ➢ 2D
- ❑ Volume Defects ➢ 3D

So, let us now proceed to defects in crystals and in this topic we will consider point defects, line defects, surface imperfection and volume defects which weak. Actually, this is itself a classification based on dimension which is 0 dimensional which are point defects, one-dimensional which are line defects, two-dimensional which are surface or interface kind of imperfections, and finally three-dimensional defects which are volume defects.

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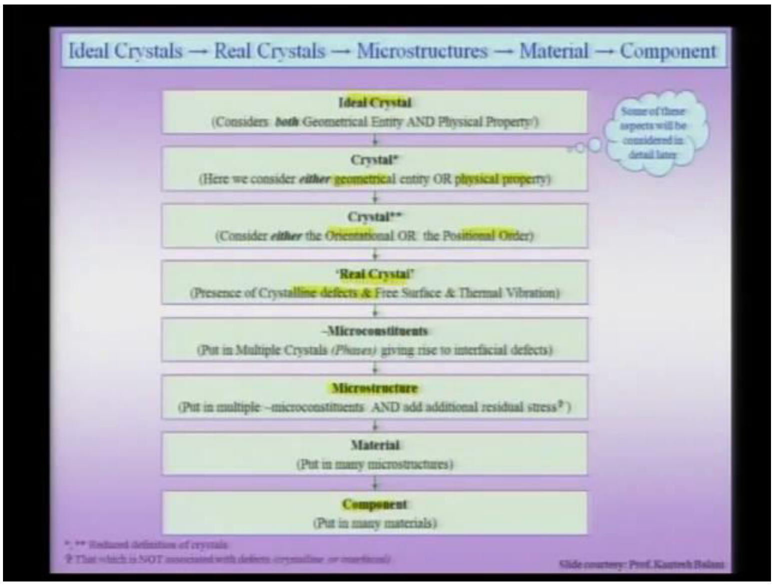

Ideal Crystals → Real Crystals → Microstructures → Material → Component

Ideal Crystal
(Considers *both* Geometrical Entity AND Physical Property)

Crystal*
(Here we consider *either* geometrical entity OR physical property)

Crystal**
(Consider *either* the Orientational OR the Positional Order)

'Real Crystal'
(Presence of Crystalline defects & Free Surface & Thermal Vibration)

~Microconstituents
(Put in Multiple Crystals *(Phases)* giving rise to interfacial defects)

Microstructure
(Put in multiple ~microconstituents AND add additional residual stress‡)

Material
(Put in many microstructures)

Component
(Put in many materials)

Some of these aspects will be considered in detail later

*, ** Reduced definition of crystals
‡ That which is NOT associated with defects *(crystalline or interfacial)*

Slide courtesy: Prof. Kantesh Balani

Now, before we actually take up some of these things will first start with the broad overview the entire what might call the classification of defects. And some of these, so that you have a broad umbrella picture of what defects are and what how do we classify them. This slide we seen before and we had already seen that we want to proceed from an ideal crystal like the case of a, which are we have seen before.

And you want to finally, arrive at for what you might call a micro structures some wherein between, and finally a component we have to go through the concept of an important modification to the ideal crystal which is now introducing crystalline defects. And now we had already seen mentioned this clearly that this defects play an very, very important role in determining the properties of a material.

In other words suppose I take and we will of course, take up these examples very soon and we will consider them in detail, but they give a very important example for suppose I took a pure crystal and I try to share it. We find that the share stress would be of the order of giga Pascal's, but suppose there are defects in this material and we had specifically talking about kind of defects which is known as dislocation. Then you would notice that the your stress would be ordered by a few orders of magnitude.

Similarly, suppose you took up very perfect ionic crystal you would notice that it would for instance it could be colourless, but suppose there are points defects known as F centres. Then you would notice that the curves could be coloured, so many, many of these properties which could range from optical mechanical to the thermal etcetera, would be very much influenced by these defects. And therefore, it is very, very important for us not only to consider an ideal crystal which have done so far.

And we also so far consider the definition of ideal crystal either based on pure geometrical entity or even a physical property. We also seen how we can sort of ignore the positional or the orientational order, we have seen that aspect also. But, now we need to go to the, what do you might call the real crystal with defects which is the first handle on understanding the properties of real materials. Before, we proceed to the other importance stage which is the stage of the micro structure.

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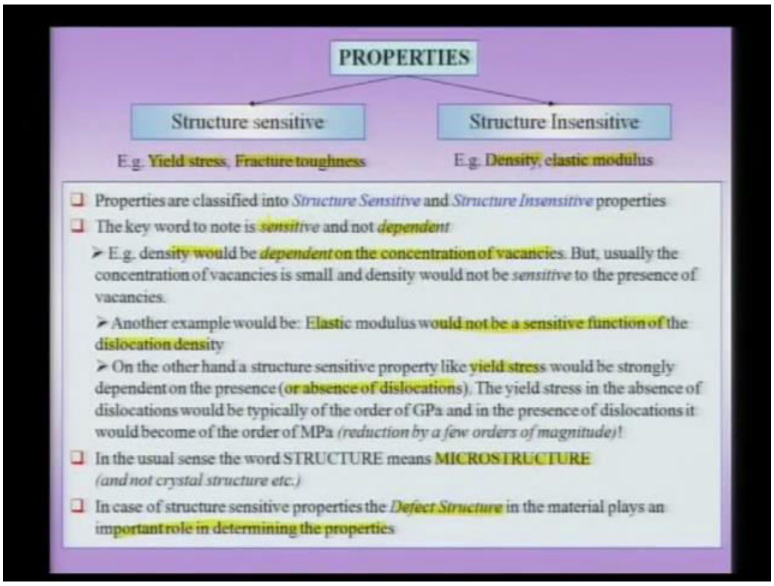

PROPERTIES

Structure sensitive

E.g. Yield stress, Fracture toughness

Structure Insensitive

E.g. Density, elastic modulus

- ☐ Properties are classified into *Structure Sensitive* and *Structure Insensitive* properties
- ☐ The key word to note is *sensitive* and not *dependent*
  - ➢ E.g. density would be *dependent* on the concentration of vacancies. But, usually the concentration of vacancies is small and density would not be *sensitive* to the presence of vacancies.
  - ➢ Another example would be: Elastic modulus would not be a sensitive function of the dislocation density
  - ➢ On the other hand a structure sensitive property like yield stress would be strongly dependent on the presence (or absence of dislocations). The yield stress in the absence of dislocations would be typically of the order of GPa and in the presence of dislocations it would become of the order of MPa *(reduction by a few orders of magnitude)*!
- ☐ In the usual sense the word STRUCTURE means MICROSTRUCTURE *(and not crystal structure etc.)*
- ☐ In case of structure sensitive properties the *Defect Structure* in the material plays an important role in determining the properties

Now, when we talk about properties there are something known as structure sensitive properties and the others which are known as structure in sensitive properties. Now, the key word of course, is the word sensitive and second key word is structure right. Now, when I say structure typically what we mean by the structure is micro structure, though in other context some people might use it.

To mean crystals structure or the electromagnetic structure, but typically when they have say structure sensitive they actually mean the word micro structure. And the key word as pointed out the sensitive; that means, that we are using the word sensitive and not dependent. To give an example for instance the density of any material would be depend on the concentration of the vacancies. Vacancies of course, as we shall see soon are missing atoms typically for in a since copper crystal, you will see that if you remove a copper atom from it is lattice point that would be called a vacancy.

Now, if you remove more and more copper atoms, you will see the density would decrease, but this is not a sensitive case of vacancies. That in see you would not change very much and normally for instance suppose you take a copper at room temperature the concentration of vacancies would be very small. And this would not be something which should be concentration vacancies would not play very important role in the determine density of the material.

So, we have to remember that often there could be properties which are dependent on the defects structure, but we are not talking about this dependences, but we are talking about the sensitivity to the presence of those defects. Another example of the dependence and sensitivity would be the elastic modulus should be a sensitive function of the dislocation density.

For instance sorry would not be a sensitive function of the presence of dislocations, but as we saw already that if you talk about in stress then the presence of dislocation plays a very important aim. Now we will talking about instance then the presence or absence of dislocation makes a lot of difference to me with regard to yield stress. So, presence of dislocation would not for instance of a density very much it would not affect by elastic modulus is very much, but it would affect by yield stress very much. And therefore, the yield strengths, yield stress would be a structures sensitive property.

And later on we shall see when we do dislocation that we not merely talking about dislocation. We will talk about details about this presence of dislocation, now they are present etcetera would also influence my yield stress. So, whenever I am talking about a structure sensitive property; that means, I need to understand my the presence of my defects in the material and how they influence my property. And example of structures sensitive properties should be as we seen already 1 is the yield stress, structures toughness should be another property.

Such, properties would be examples of the density elastic modulus etcetera. Now, in toriently or ardently we had talked about defects and we used a term perhaps in this conjunction which is very important term to understand the term of defect structure. For instance, now if you read the last sentence here in case of the structure sensitive properties the defect structure in the material plays an important role in determining the properties. So, there is an important technical term or a technical phrase which comes in this context which is not get defects, but defect structure.

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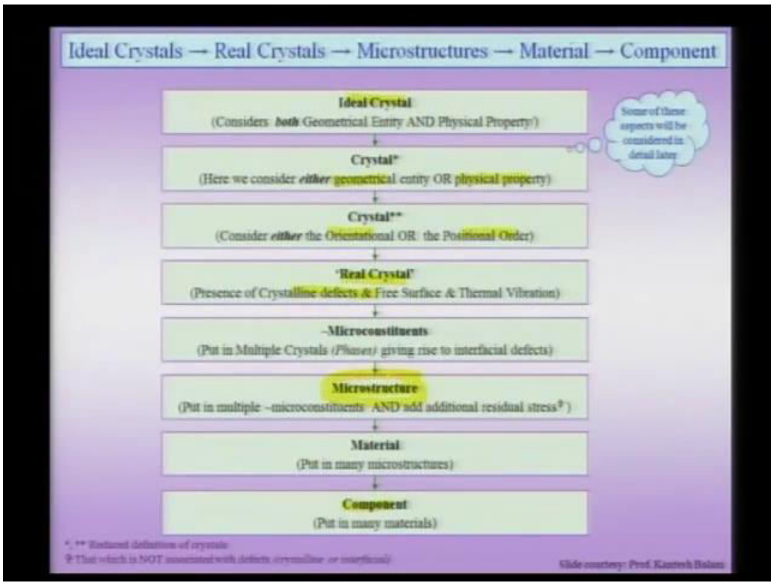

Ideal Crystals → Real Crystals → Microstructures → Material → Component

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(Here we consider *either* geometrical entity OR physical property)

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(Consider *either* the Orientational OR the Positional Order)

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*, ** Relaxed definition of crystals
† That which is NOT associated with defects (crystalline or interfacial)

Slide courtesy: Prof. Kantesh Balani

So, if you will go back to the diagram before you can start with crystals. Of course, you can talk and then talk about the defected or crystals which means there are defects inside, but then we go to the next skill which is known as micro structures. So, this is an important thing we saw micro structure right.

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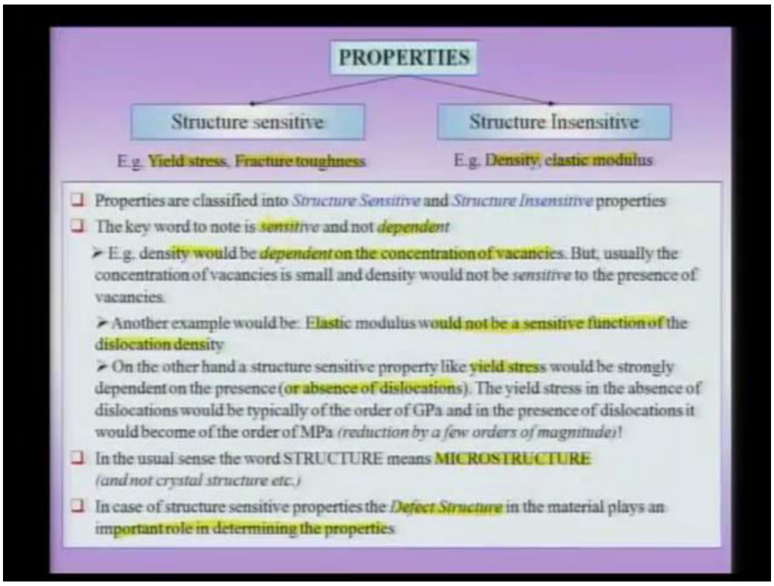

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Similarly, we know do not want to just we talking about the defects, but we want to use a more sophisticated language which is the concept of defects structures.

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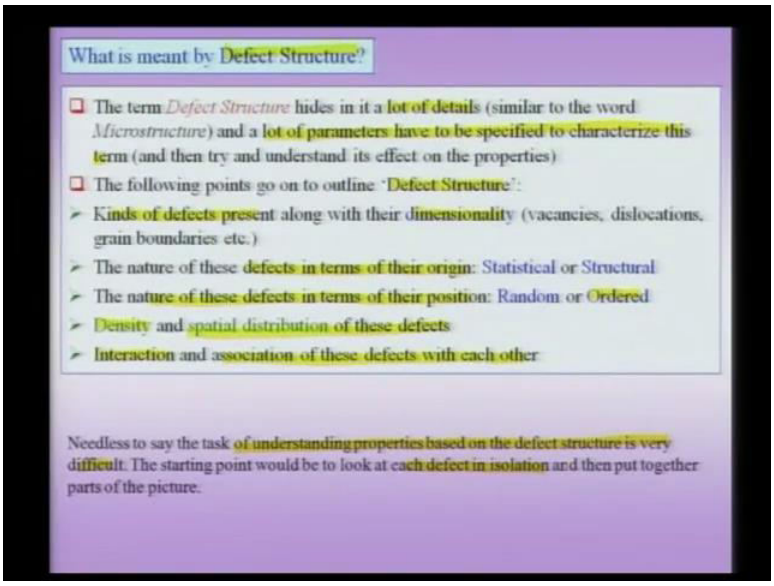

What is meant by Defect Structure?

- ☐ The term *Defect Structure* hides in it a lot of details (similar to the word *Microstructure*) and a lot of parameters have to be specified to characterize this term (and then try and understand its effect on the properties)
- ☐ The following points go on to outline 'Defect Structure':
- ➢ Kinds of defects present along with their dimensionality (vacancies, dislocations, grain boundaries etc.)
- ➢ The nature of these defects in terms of their origin: Statistical or Structural
- ➢ The nature of these defects in terms of their position: Random or Ordered
- ➢ Density and spatial distribution of these defects
- ➢ Interaction and association of these defects with each other

Needless to say the task of understanding properties based on the defect structure is very difficult. The starting point would be to look at each defect in isolation and then put together parts of the picture.

So, what do we mean by this defect structure of course, initially we will start a description of defects. We will start with the isolated defects may be a single vacancy or a single dislocation. To understand what this defects is or what role does it play in altering the symmetry of the crystal or it is properties, but soon we will have to understand not isolated defects, but defects structures.

So, what is this defect structure actually, it is a very complicated phrase to understand. It hides inside it lot of details and I may in some sense very similar as I pointed out to the term micro structure which also hides in a lot of details. And a lot of parameters actually have to be specify to characterise this term. And of course, the bigger goal would be not only to understand the defect structure, but to correlate the properties. Exactly, the same way not only we want to describe the micro structure, but we want to correlate the micro structure to the properties.

What would typically we call the structures property correlation or the micro structure property correlation. Now, of course, this initial description of we highly sufficient to understand entire term defect structure, but we will try to see what points go into the definition of the term defect structure. Now, I need to understand that what kinds of defects are present along with the dimensionality.

So, I need to understand say for instance if their vacancies or their dislocations or their grain bond which are present my crystal now or which go on to break my crystal or break up perfect symmetry in the material. And therefore, I need to understand kind of defects present along with the dimensionality, I need to also understand the nature of these defects in terms of the origin. And will of course, take up some of these topics very soon some of them slightly later, but we will try to understand these terms which of course, are the key words for our future discussions.

So, I need to understand the nature of these defects in terms of the origin or they originating from or they statistically present or they are have the structure origin. This is an important question I would ask, because now that would directly have an influence on the distribution of these defects in the material, as well apart from the role in the defective play on it is properties. I need to understand the nature of the defect in terms of their position, for instance or they random defects present some wherein the crystal.

So, there are no particular positional order or they could be even be ordered. Like, exactly the same way we have describe for instance the ordering of alloys. So, these defects also could get order and therefore, I would have an ordered crystal now, but now the entity which is getting ordered is not a atomic species, but actually a defect. And this where very, very important and we saw that ordering actually will leads to a change symmetry of the structure. And actually the structure itself the very recent example we construct was a orientational order with respect to the fullerene crystal.

And similarly when defects get ordered change the symmetry of the crystal and the crystal structure and correspondingly the properties. I obviously, need to understand density of these defects and this spatial distribution of these defects. So, this is very important quantity suppose I am talking about vacancies it is not enough, I know for instance there are vacancies present in the material I need to know. How many of these lattice sites fraction of these lattice sites are vacant; that means, I need to know density.

I also need to know what is the spatial distribution of these vacancies? In others words suppose are these vacancies even distributed in the crystal or they for instance associated with each other forming a di-vacancy or many of these vacancies coming together in a particular crystallographic plane. See their questions we would like to ask and no all the questions become very important and particular in the description of defects and understanding the term defect structure.

I need to understand the interaction association of these defects with each other, suppose I have a defect like for instance interstitial impurity atom. I need to ask this question where is this interstitial impurity atom for instance position with respect to a say for instance grain boundary say with respect to a dislocation line. So, these are questions I would ask and therefore, for instance if interstitial impurity atom is goes positioned very near dislocation, it would get into the low energy configuration.

And now these 2 defects get associated, similarly vacancies could get associated to form a di-vacancy. And what is the kind of interaction I am talking about between these defects? How does the point defect interact with a dislocation? How does a point defect interact with a grain boundary? So, these are questions I would ask and therefore, I need to worry about the interaction and association of these defects with each other.

So, needless to say the task of understanding these properties based on defect structure is very difficult. So, this is a actually a very, very difficult proposition, but then the starting point is very, very easy that I start with each defect in isolation. And then slowly start putting some of these defects together to understand the bigger picture.

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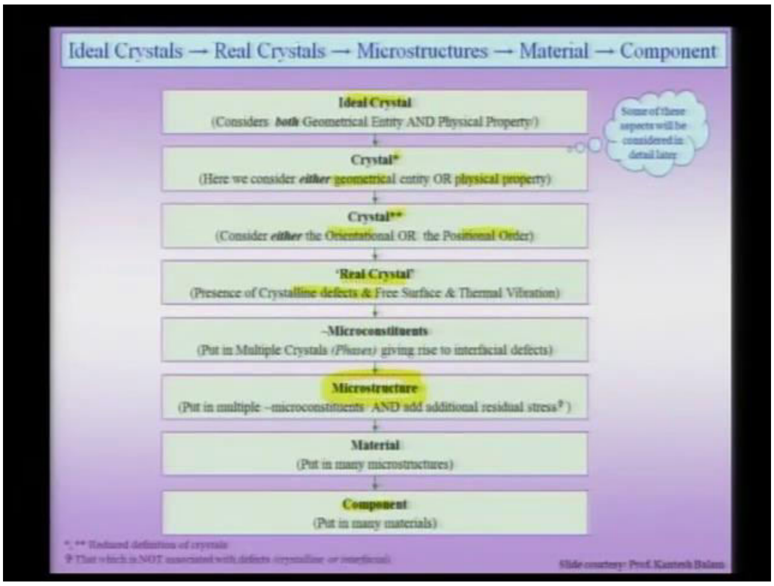

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(Here we consider *either* geometrical entity OR physical property)

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$\ddagger$ That which is NOT associated with defects (crystalline or interficial)

Slide courtesy: Prof. Kantesh Balani

So, let me summarize this very, very important slide because this slide tells you that I am starting with a perfect crystal. Of course, the way I define this perfect crystal we have already seen that it could be not just a perfect I could mean in some of these reduced definitions which I had shown by starts and double stars here.

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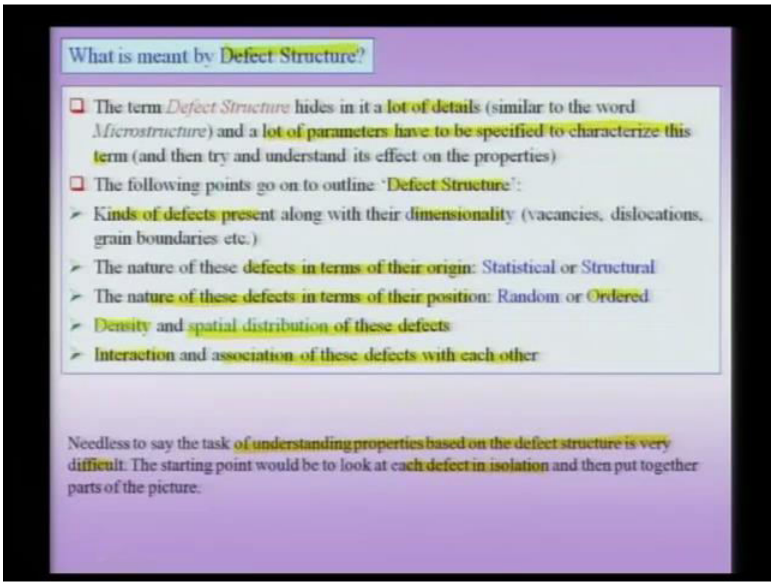

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Needless to say the task of understanding properties based on the defect structure is very difficult. The starting point would be to look at each defect in isolation and then put together parts of the picture.

But, no sooner than later I would like to proceed to real crystals wherein I introduce defects. 1 inevitable defect; obviously, is going to be the surface because no crystals infinite. Therefore, I need to truncate the crystal some point of time and therefore, I would have finite crystals. So, 1 inevitable defect we already seen the other inevitable defect would be thermal vibration, because 0 Kelvin is unattainable. Therefore, at any positive Kelvin there are going to be some vibrations of atoms around their mean position's the lattice position.

Therefore, thermal vibration is another unavoidable defect therefore, 2 defects are unavoidable materials anywhere. Therefore it is better that I consider real crystals sooner than later, but I am talking about real crystals; that means, I am introducing defects. I cannot talk about defects in isolation I and or I need to characterize the defects a little more detail before I understand the properties.

Therefore, I need to understand the term called defect structure and I am talking about a defect structure I am talking about the density of these defects, the spatial distribution of these defects, the kinds of defects present. What is the origin in terms of for instance the or they structural in origin or they are ordered for instance are they disordered. So, I need to understand all these little details before I can understand the defect the role the defect plays in my properties.

And once I have in this understanding I am really in a position for instance to jump to some of the next level which would be understanding microstructure in it is entirety and also the for instance the behaviour of a component. Now, as I pointed out to gain that we shall always start with the simplest possible; that means, we will start with the single isolated defect try to understand it is behaviour in the crystal and slowly go on to understanding this more complicated cases of defects and material.