

**Modern Construction Materials**  
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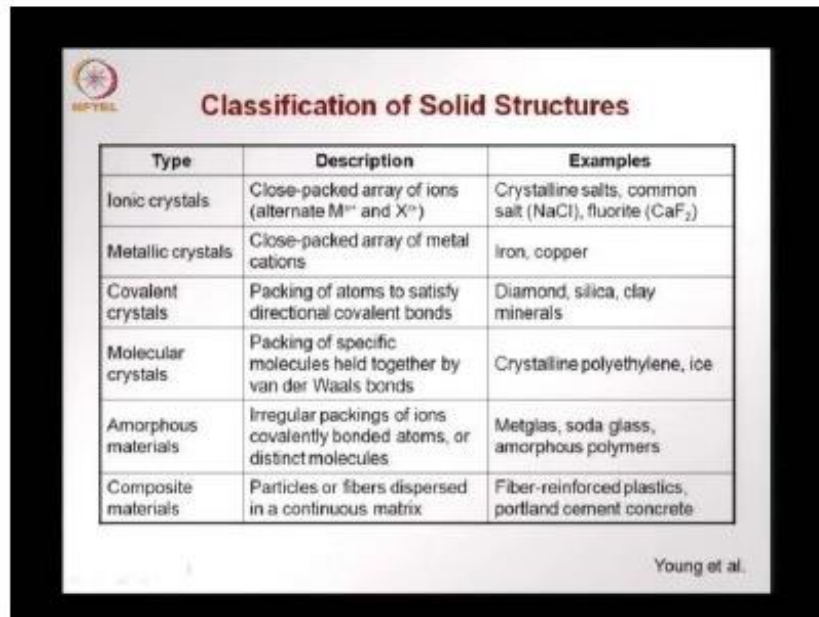
**Module - 2**

**Lecture - 3**

**Structure of solids - I**

Welcome to the third lecture on Modern Construction Materials. We looked at atomic bonding and how chemical bonds are formed, in the previous lecture. These chemical bonds lead to certain structures in materials that we are going to discuss later. Today we are going to look at structure of solids. As you know, there are different phases of matter: solids, liquid and gases. We are going to look at the crystalline structure of certain materials. Later on we will look at defects that occur in these crystalline structures. We will also look at materials which are not crystalline i.e. they are glassy or amorphous.

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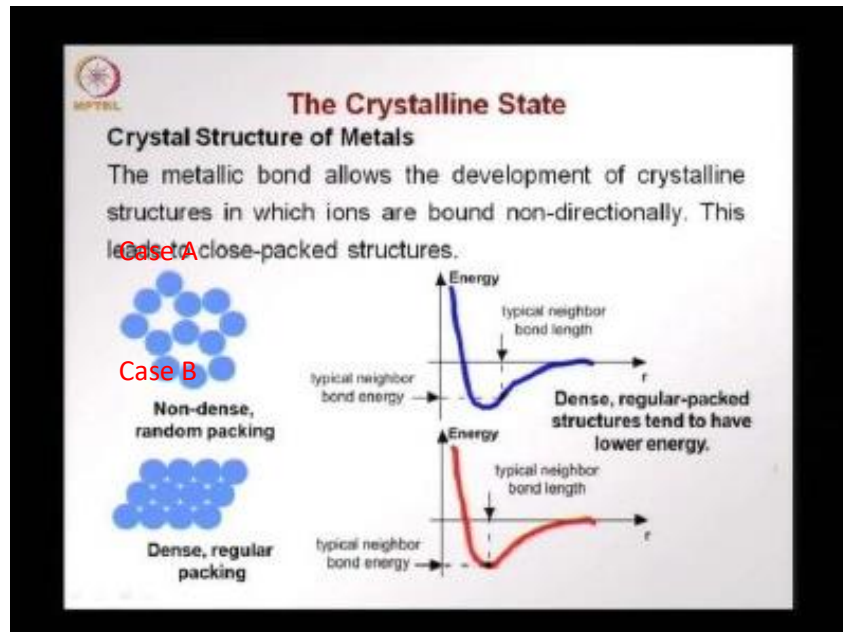
Type	Description	Examples
Ionic crystals	Close-packed array of ions (alternate $M^{n+}$ and $X^{n-}$ )	Crystalline salts, common salt (NaCl), fluorite ( $CaF_2$ )
Metallic crystals	Close-packed array of metal cations	Iron, copper
Covalent crystals	Packing of atoms to satisfy directional covalent bonds	Diamond, silica, clay minerals
Molecular crystals	Packing of specific molecules held together by van der Waals bonds	Crystalline polyethylene, ice
Amorphous materials	Irregular packings of ions covalently bonded atoms, or distinct molecules	Metglas, soda glass, amorphous polymers
Composite materials	Particles or fibers dispersed in a continuous matrix	Fiber-reinforced plastics, portland cement concrete

Young et al.

When we look at the different types of solid structures, we have ionic crystals, materials which form through ionic bonds, where we have arrays of ions of different charges (positive and negative charged ions), and these form ionic crystals such as those that we find in salts like common salt, fluorite and so on. In metallic crystals, we have metal cations that are closely packed, and this is what we see in metals including iron, copper and so on. In covalent materials also, we can have crystalline structures, when we have chains, sheets or three dimensional networks, where there is packing of atoms and this gives a crystalline structure. The examples are silica, diamond, clay minerals and so on.

We can also have molecular crystals, where we have molecules held together by Vander Waals or hydrogen bonds. They are packed together in specific configuration, and this we find in plastics such as polyethylene and other materials such as ice. One thing that is common in all crystalline materials is that there is an ordered structure. There is an arrangement that is repetitive, and there is a dense packing. There are other materials which are not crystalline, and they are generally called amorphous materials, where you do not see a regular packing, but there is an irregular arrangement of ions, atoms or molecules. Examples are glass and polymers that are amorphous. And also some materials which are generally crystalline could be transformed to amorphous materials such as metallic glasses. The last class of solid structures is composite materials, where we have different phases mixed together, like one set of particles of fibers dispersed in a continuous matrix (like we have in fiber reinforced plastics) or we have aggregates or particles disposed in a cementation matter (like we have in Portland cement concrete).

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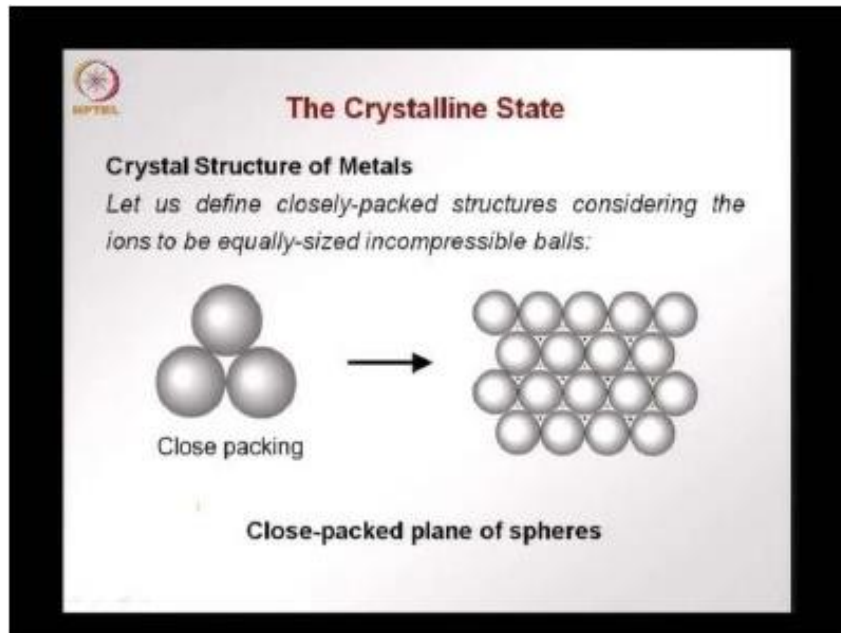


We will start with the crystalline structure of metals. The metallic bond, as we saw in the previous lecture, allows the development of ordered crystalline structures which have cations (positively charged ions) that are bound in a non-directional manner.

That means that they are formed symmetrically and they grow in all directions. This can lead to closely packed structures. So, here we have a structure that is not so closely packed (Case A). There is no dense arrangement, it seems to be a random packing. And if you go back to the Condon-Morse diagram that we looked at in the previous lecture we find that here (blue), we would not be at the bottom-most point of the curve which signifies the minimum energy, but the separation now between the particles is more. So, we find that the inter particle separation is not  $r_0$  corresponding to the minimum energy, but a little bit higher. A material will always try to reach the minimum state for stability. This always happens in all materials. When we look at the structure, the structure will try to get the minimum energy level possible that makes it more stable. So, if we compare this case to another case where there is a dense regular packing (Case B),

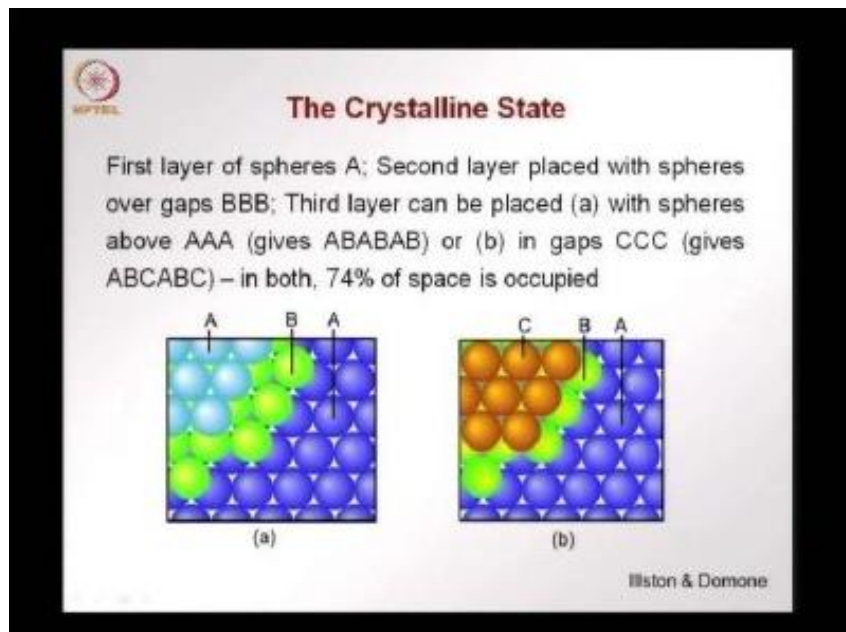
you see that the particles are closer to each other. And when we go back to the Condon-Morse diagram, here that we have in red, we find that we will have a lower energy because the particle packing is such that the inter particle spacing is lower and you reach the most stable state or the minimum energy level. This is the reason why, we have dense structures, because we have regular packing that leads to lower energy, because each particle is surrounded by several neighbors and the packing becomes regular and dense.

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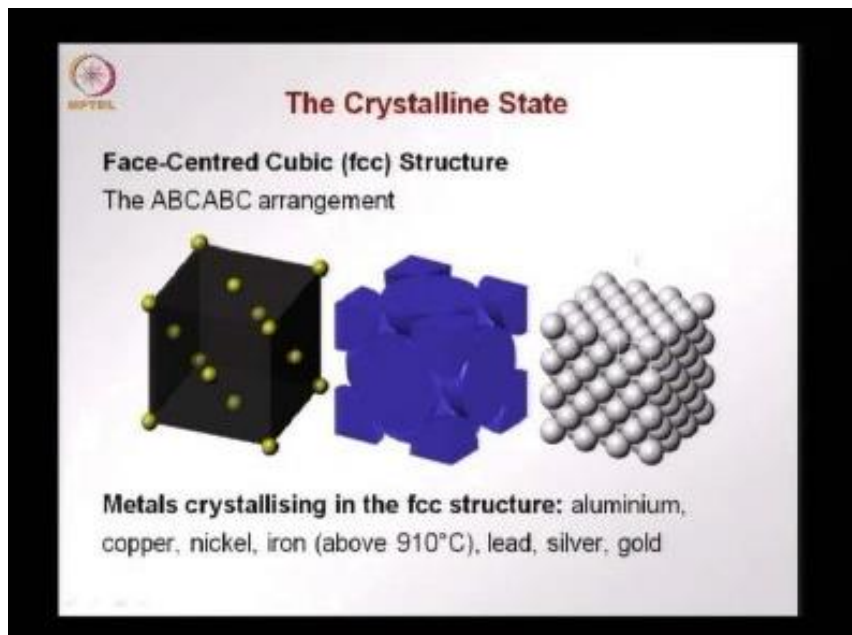
Now let us see how the packing can be achieved in such a structure. Suppose we take ions and we represent them by spheres, and we try to see how they can be closely packed like we see in this diagram. For simplicity, we are considering all the ions to be equi-sized incompressible balls. We can now put a layer or a plane of spheres as shown. So, this would achieve a very compact structure which will give the least energy possible.

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Now we have two other layers. We can have a couple of cases. Let's say in the first one, we have what we looked at in the previous slide- the spheres aligned together in one layer that is the layer-A. We can have the next set of balls placed over the gaps in the layer-A, that is the layer-B; after that we can have two choices, one could be putting the next layer on top of position of balls in layer-A. So that is what is called a structure ABABAB. So, this is the repetitive A and B structure. Or you can have this case, where we put this spheres over the gaps on B, so that gives the spheres located in C giving a structure what is called ABCABC. So, these are two possible structures, where you can have dense packing. In both of these cases, 74 % of the space is occupied. So, this is one way to get dense packing and this we see in many materials.

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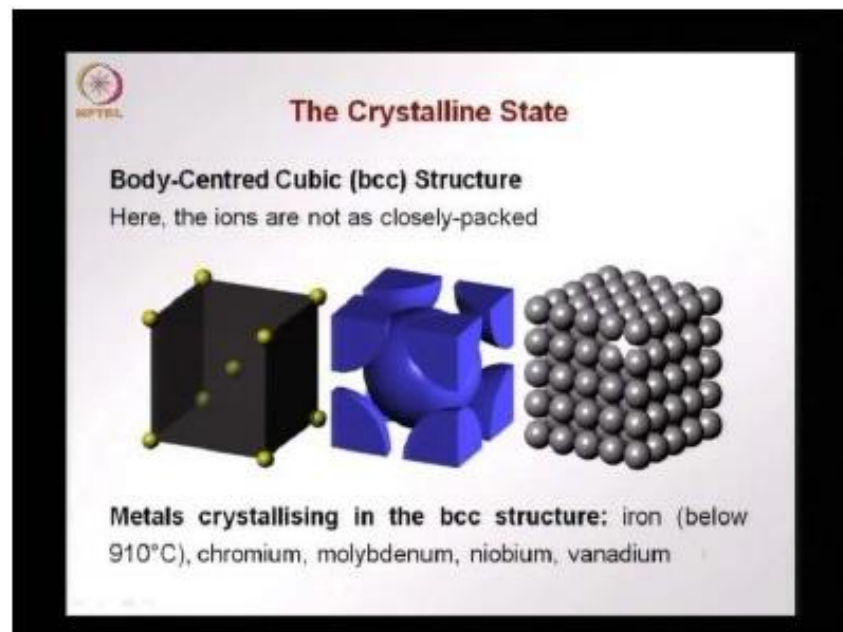
The ABABAB arrangement is called the hexagonal close packed structure or the hcp structure. We see this in metals such as magnesium, zinc, cadmium, cobalt and titanium. You see the structure here, this is called hexagonal close packed structure - the hcp structure, where we have an arrangement in hexagonal nature and each particle is surrounded in its plane by six other particles (or cations in the case of metals).

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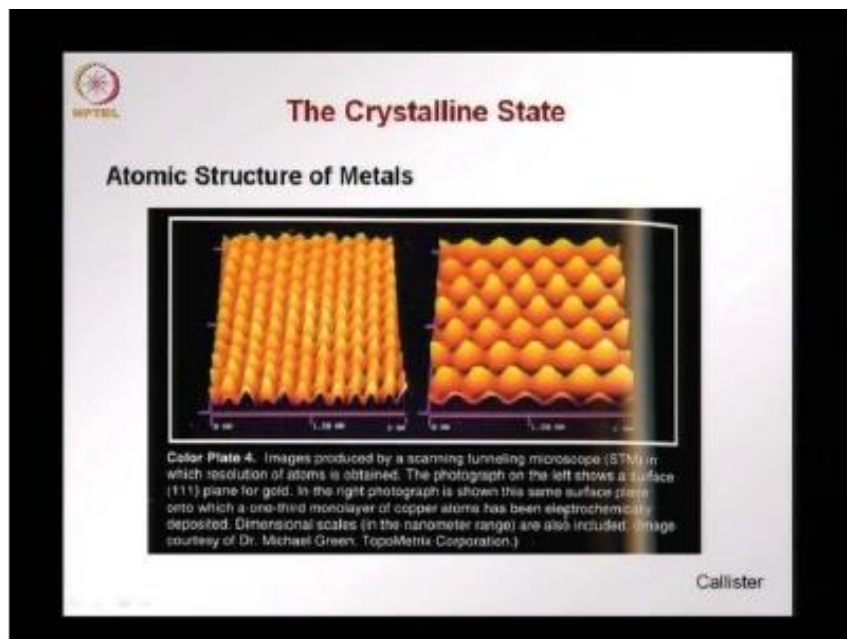
The other arrangement, the ABCABC arrangement, leads to what is called the face centered cubic structure, where we have any atom or particle surrounded by particles on its plane and top also. And if you see here, you see a cube formed here by the different particles, so this is called face centered cubic structure. The metals that are crystalline in the fcc structure include aluminum, copper, nickel, lead, silver and gold. Iron exists in this structure above 910 OC. It goes through a phase change at 910 OC. Above this temperature, iron exists in the face centered cubic structure.

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You can also have sometimes structures that are not as closely packed. We saw that in previous two cases 74% of the space was occupied when we consider spheres put together in the two structures what we discussed. We can have something called a body centered cubic structure, where we have each sphere touching eight other spheres below and above. The parts of the eight spheres that are touching it are shown. This is called a body centered cubic structure, where we have a particle in the middle and then you have cubic structure around it. Here the particles or the ions are not as closely packed as in the previous two cases we saw. Metals that crystallize in the bcc structure are chromium, molybdenum, niobium, vanadium and iron below the 910 0C. As I told you before, iron goes through a phase change at 910 0C. Below that, iron also has bcc structure.

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Now this is not just a model, but in reality, we have evidence that the structure of the metals is of this nature. These are couple of pictures taken from the book of Callister, where we see images of atoms produced by scanning tunneling microscope. We have on the left hand side a plane of gold. What you see there as bumps are gold cations. On the right-hand side again we see a layer of copper atoms. And again, these spherical bumps that you see are atoms of copper in the nanometer scale. So, this actually is the structure of metals and that has been visualized in the previous slide in the form of spheres to make the point about the crystalline nature.



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**The Crystalline State**

**Why the Different Structures?**

- The structure adopted is that which gives the crystal the least internal energy.
- A crystal structure that has the least energy at one temperature need not necessarily have the least energy at another temperature.
- The change in structure brought about by temperature (e.g., in iron) forms the basis of metallurgy.

Ilston & Domone

We already looked at different types of arrangements in crystals. Why do we have different structures? Well, the structure adapted is that which gives the crystal the least internal energy. If you remember the discussion on the Condon-Morse diagram, we said that always the structure will be such that the lowest energy is achieved. And for that, there is a certain inter particle distance or intermolecular distance. And the structure will be that which gives the crystal the least internal energy, for the condition that the crystal is in.

Now a crystal structure that has the least energy at one temperature need not necessarily have the least energy at another temperature. We already saw the example of iron which changes its structure at 910 0C, having a structure above and a structure below the temperature. So, a crystal structure for one temperature need not give the least energy for any other temperature, and this changes the structure. For example, what we saw in iron forms the basis of metallurgy, which deals with the transformation of the structure and forms of materials.

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**The Crystalline State**

**Ionic Solids: Ions of the same charge**

- Ionic crystal structures are packed arrays of anions with cations located in the holes of the array.
- The geometries depend on the radius ratio,  
 $R = r_{\text{cation}} / r_{\text{anion}}$

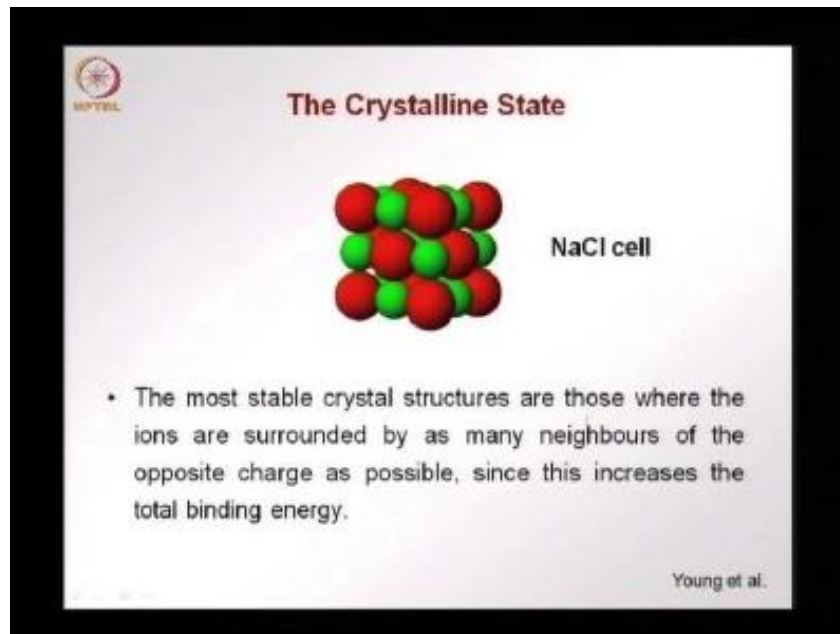
A B C

$r_{\text{cation}}/r_{\text{anion}} > \text{ideal}$   $r_{\text{cation}}/r_{\text{anion}} = \text{ideal}$   $r_{\text{cation}}/r_{\text{anion}} < \text{ideal}$

Stable Stable Unstable

Ionic solids also have crystalline arrangement. In ionic solids, we have ions of same charge packed in layers. So, you have in ionic crystal structures, arrays of anions with cations in the holes of the array. So, the arrays are made of anions and the cations fit into the holes between the anions. The geometry which results depends on the ratio of the radii of the cations and anions; that is the ratio between the radius of the cations and the radius of the anions. The best case or the most stable case is this (B), where you have the cations fitting exactly in the hole between the anions. So, all the particles are touching each other. It gives a close packing and a stable structure with the least energy. This is also stable (A), because there is not much possibility for movement. But this is above ideal, the ratio is above ideal. This is an unstable situation (C), where you have cation which is much smaller than the space between anions and this give rise to an unstable structure and this will not last for a long time.

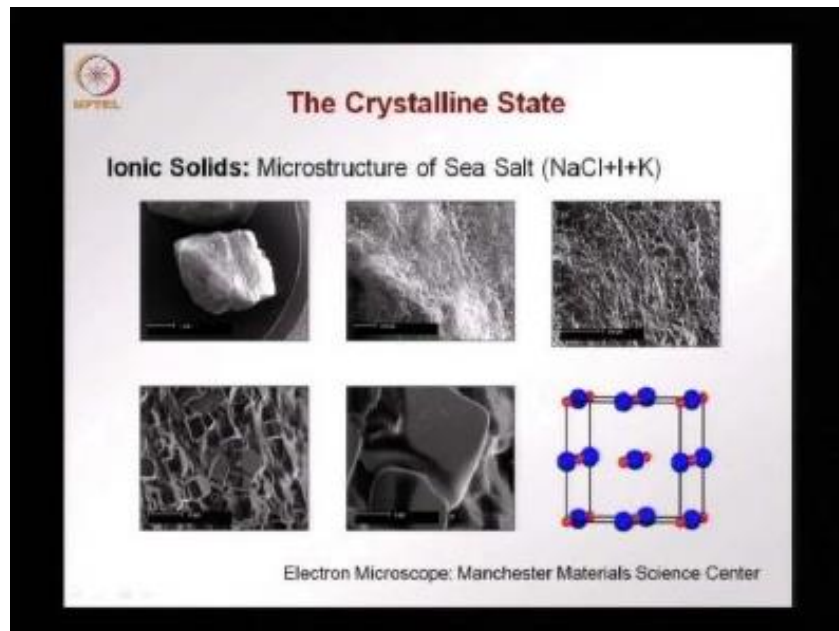
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So, we continue to look at ionic materials and an example is sodium chloride - common salt, where we have the sodium and the chloride ions distributed in an orderly structure. And the most stable structures are those where, as I said before, the ions are surrounded by as many neighbors of the opposite charge as possible (This increase the binding energy and the attractive energy that keeps the solid together). It increases the total binding energy and it decreases the potential energy to a minimum. That is when the material is most stable.

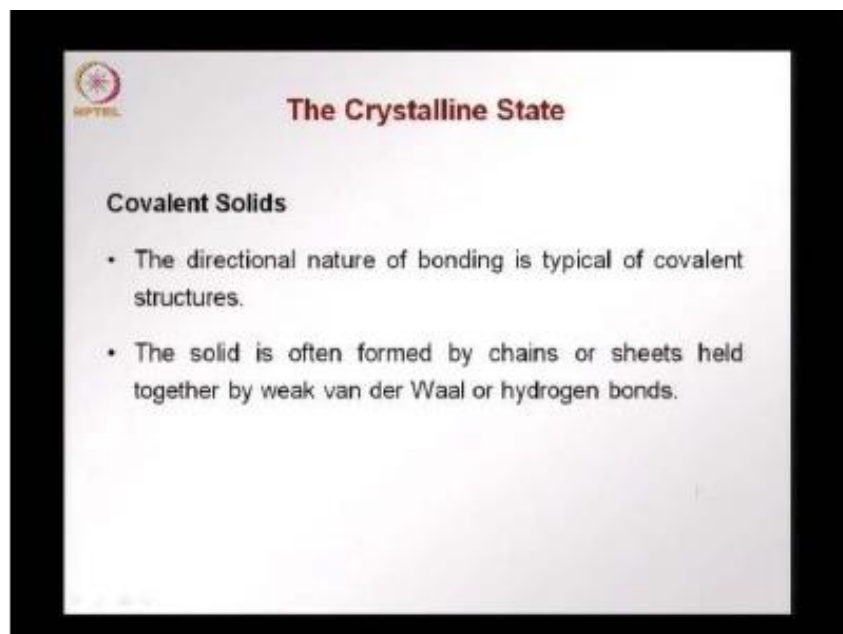


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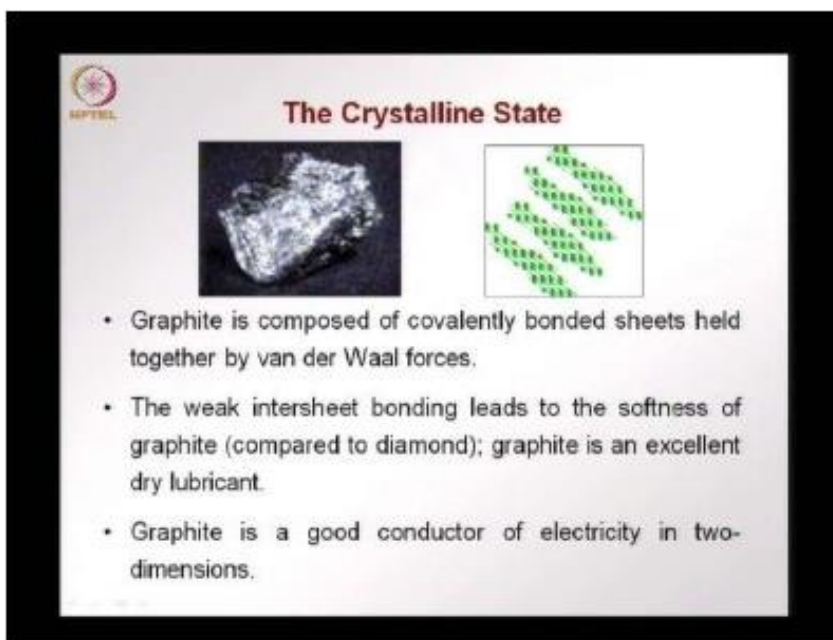
Now again, there is evidence for this, that we can get from a microscope. These are different images taken from the site of Manchester Material Science Centre. And here you see grains of sea salt at different scales. On the left top you see a grain of sea salt. And next to it is an image that is closer. The bar that you see here is about few hundred microns. This is a closer image. Again you see some of the grainy texture on the surface. When you go down, this is now a scale of 20 microns; you see neat cubic crystals of salt like what we saw before in the schematic diagrams. You see here the crystals of salt and one crystal in the size of about 5 to 10 microns. So, you see here how the crystal of sea salt is formed and this is similar to what we idealized in the diagrams before. So, there is quite a lot of evidence from microscopy as to how these structures exist in the micro scale. And now from what we have learned in atomic bonding, we can understand how the structure forms and how it can lead to crystalline or orderly structures.

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We go on next to the third type of bond that we studied in the previous lecture - covalent bond, and covalent solids. We also know that covalent bonds are directional bonds. As opposed to what we saw in ionic and metallic bonding, covalent bonds are directional. And this is very typical of covalent structure. We saw in the previous lecture that covalent structures have chains or sheets. Within the chains and sheets you have covalent bonds; and across them or between the chains and sheets, you have weak Vander Waals or hydrogen bonds. So, within the chains, you have covalent bonds and between the chains and between the sheets, you have weak Vander Waals or hydrogen bonds holding them together. Only when there is an orderly structure of the chains and sheets, we have a crystalline covalent solid.

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The slide, titled "The Crystalline State", features a photograph of a piece of graphite on the left and a diagram of its layered structure on the right. The diagram shows several parallel sheets of carbon atoms, each represented as a hexagonal lattice of green spheres. The sheets are held together by weak van der Waals forces, indicated by small arrows between the layers.

- Graphite is composed of covalently bonded sheets held together by van der Waal forces.
- The weak intersheet bonding leads to the softness of graphite (compared to diamond); graphite is an excellent dry lubricant.
- Graphite is a good conductor of electricity in two-dimensions.

Graphite is an example of where we have covalently bonded sheets. A piece of graphite is shown. Within it, we see that the carbon atoms are all aligned as sheets in an orderly manner. These sheets are held together by weak Vander Waals forces. This type of structure gives graphite a lot of interesting properties. One is the softness coming from the weak inter sheet bonding the sheet slip one over the other. This makes graphite an excellent dry lubricant, because the weak Vander Waals forces can be overcome. The Vander Waals bond can be broken easily and sheets start slipping one over the other. Now you can have carbon with covalent bonds forming a very hard structure also. The example is diamond.

In diamond, you have a network of covalently bonded atoms giving a hard strong structure as opposed to the same element carbon in graphite, which gives a soft nature because sheets are formed. So, to recap, graphite is formed in layers of carbon. Within the layers, you have covalent bonds and across, from between one sheet and other, we have Vander waal's bonds. Because of this, we have good electrical conductivity along the sheets and graphite is a good conductor of electricity in two-dimensions; (i.e.) along the sheets, not across them.

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**Silica and Silicates**

- The silicate tetrahedron is the basic repeating structure of silica and the silicates. The tetravalent silicon ion is surrounded by 4 oxygen anions, resulting in  $(\text{SiO}_4)^{4-}$ .
- The negative charge is neutralized when the oxygen anions are shared with other silicate tetrahedra or other cations.

The Silica Tetrahedron

Silicate chains

Legend: Oxygen (blue), Silicon (yellow)

Detailed description: The slide features a title 'Silica and Silicates' at the top. Below the title are two bullet points explaining the silicate tetrahedron and how its negative charge is neutralized. At the bottom, there are two diagrams. The left diagram, titled 'The Silica Tetrahedron', shows a central yellow sphere (silicon) bonded to four blue spheres (oxygen) in a tetrahedral arrangement. A legend below it identifies the colors: blue for Oxygen and yellow for Silicon. The right diagram, titled 'Silicate chains', shows a series of silicate tetrahedra connected by sharing oxygen atoms, forming a chain structure.

Another set of materials that are covalent solids are based on silica and silicates. The silicate tetrahedron that we saw in the previous lecture is a basic repeating structure in silica and silicates. The silicon ion is surrounded by four oxygen ions, resulting in  $(\text{SiO}_4)^{2-}$  with a charge imbalance of -4. This charge is neutralized when the oxygen anions are shared with other silicate tetrahedra to form chains and sheets. So, this is the silica tetrahedron with one atom of silicon in the middle surrounded by four atoms of oxygen (bottom left) and this can now link to form silicate chains (bottom right).

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**Silica and Silicates**

single chain

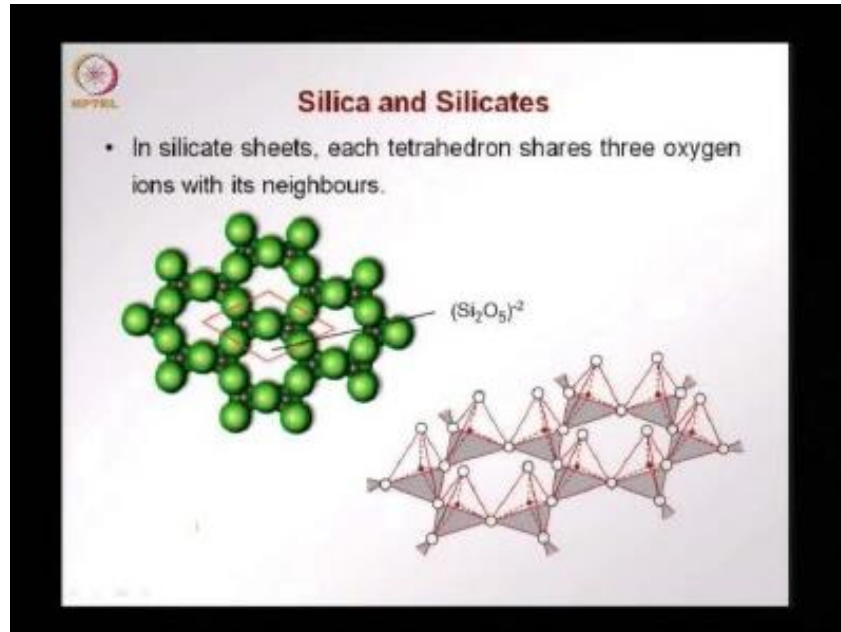
double chain

*Certain double chain silicate structures form long thin crystals that can be bent and made into fabric, such as asbestos.*

Detailed description: The slide features a title 'Silica and Silicates' at the top. Below the title are two diagrams. The left diagram, titled 'single chain', shows a vertical chain of silicate tetrahedra connected by sharing oxygen atoms. The right diagram, titled 'double chain', shows two parallel chains of silicate tetrahedra connected by sharing oxygen atoms. At the bottom, there is a paragraph of text: 'Certain double chain silicate structures form long thin crystals that can be bent and made into fabric, such as asbestos.'

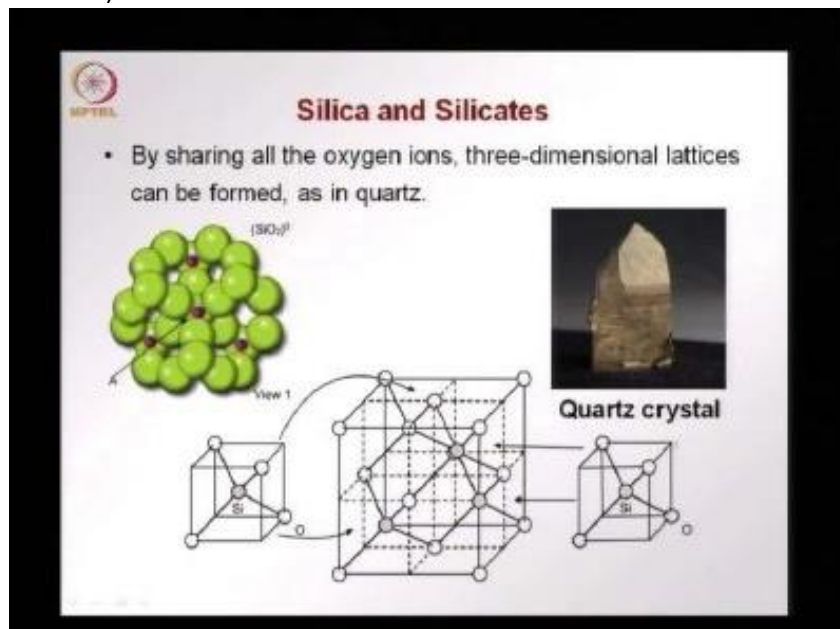
You have two types of chain that can form. You have single chain or we can have double chained structure. In either case, what we find is that long thin crystals are formed and these can be bent and made into fabric or a fibrous structure. One example is asbestos. As you know, it has been used for a long time for insulation, for reinforcing cement composites and so on. Now it is not in much use because it is harmful to health. At one period of time, asbestos was a very popular reinforcing and insulating material that was used in Civil Engineering.

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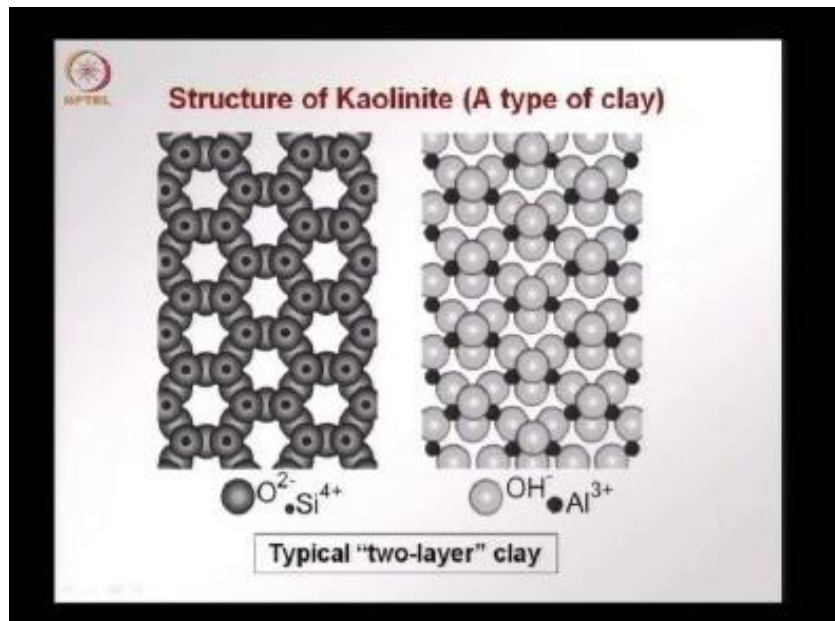
also can form Now, the tetrahedral into sheets. So you have a sheet structure, where each tetrahedron shares the oxygen ions with its neighbors, forming these sheets. So, this sheet structure is formed by the tetrahedron.

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You can also have these tetrahedra making a three dimensional lattice. This is one of the exceptional covalent materials which has a three-dimensional structure, the other being diamond, which forms a three-dimensional structure with carbon. Now we have lattices of the silicate tetrahedra which can form a network structure like in quartz. So, quartz is a crystalline material that is made up of this tetrahedron forming a network structure like this (shown in slide).

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Now one type of crystalline material that we find in nature is clay. This is the structure of Kaolinite, a type of clay which has a two layered structure. One layer is made out of the silica tetrahedron (tetrahedral sheets). On top of this, we find an aluminum hydroxide sheet which is octahedral. This fits in and takes care of charge imbalance, and together they form units that are neutral.

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**Structure of Kaolinite**

- Kaolinite  $[Al_2Si_2O_5(OH)_4]$  can be visualised as having layers of tetrahedral  $[Si_2O_5]^{2-}$  fitting together with layers of octahedral  $[Al_2(OH)_4]^{2+}$  through ionic bonds.
- The charge and the geometry of the two sheets match perfectly to form 0.7 nm thick sheets.
- The sheets are bound to each other by van der Waal forces.

So, Kaolinite can be visualized as layers of tetrahedral ( $\text{Si}_2\text{O}_5$ )<sup>2-</sup>, linking up with layers of octahedral aluminum hydroxide  $[\text{Al}_2(\text{OH})_4]^{2+}$ . Both have charge imbalance- the tetrahedral has a -2 charge imbalance and octahedral aluminum hydroxide has +2 charge imbalance. So, they have an ionic bond which forms between the layers to give a single unit. So, the charge geometry fits/ matches each other and together the two sheets form a 0.7 nanometers thick sheet. Very thin sheets occur within kaolinite. Now different sheets are bonded to each other by Vander Waals force, which is the weak point. Between the tetrahedral sheets and the octahedral sheets we have ionic bonds. But between this unit which forms as sheets and the next one, we have weak Vander Waals forces which are not very strong.

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**Structure of Kaolinite**

$\text{Si}_2\text{O}_5^{2-}$

$[\text{Al}_2(\text{OH})_4]^{2+}$

Weak van der Waals bonding between layers

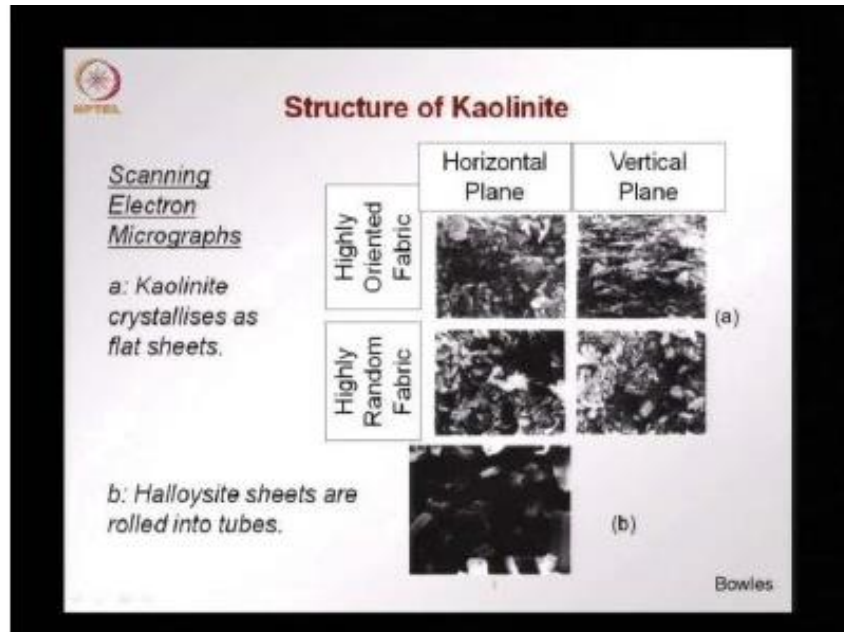
- Kaolinite crystallises as flat sheets. It does not absorb water but adsorbs it as a thin external layer.
- Halloysite  $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 4\text{H}_2\text{O}]$  has a similar structure but with water between the sheets.

Young et al.

So, this is what is shown, you have one unit made up of  $(\text{Si}_2\text{O}_5)_2^{2-}$  and  $[\text{Al}_2(\text{OH})_4]^{2+}$ . Between this unit and next you will have weak Vander Waals forces which are not very strong. So, that is why these sheets can split along this direction. You can have the separation of these layers in Kaolinite. It crystallizes as this flat sheet, but does not absorb water. But, it can adsorb water as a thin external layer in the surface. It is a type of clay which does not absorb water or expand. Another similar material is Halloysite which has water between the sheets, as opposed to what we see in Kaolinite.

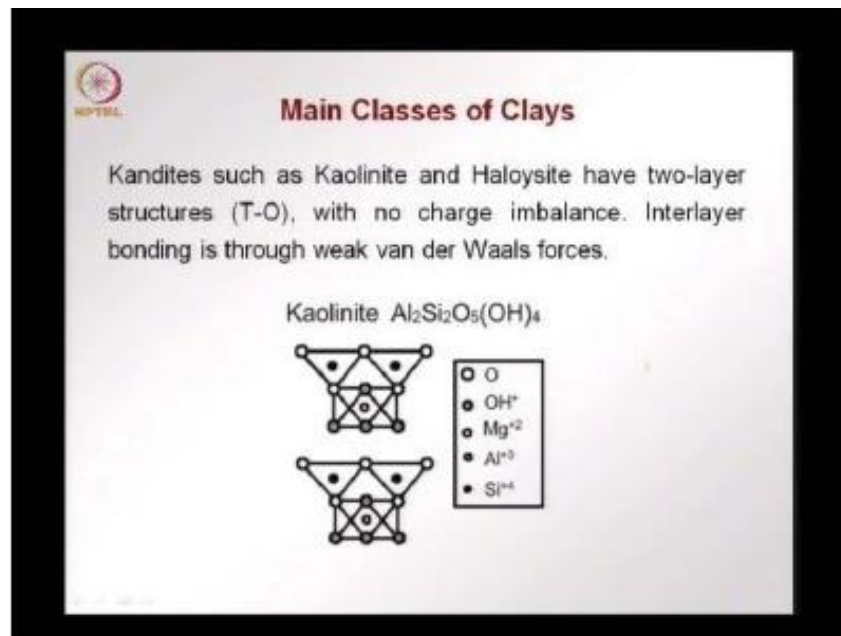


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These are some scanning electron micrographs taken from book of Bowles, where we see the small platelet or crystals which form in Kaolinite (a). These are the small sheets which make up Kaolinite. Halloysite is more of a tubular structure. We can see some tubular structures here (b) because the Halloysite sheets are rolled like tubes. Whereas, Kaolinite crystallizes into small flat sheets.

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There are three main classes of clays. What we have discussed up to now is a group called Kaolinites which includes Kaolinite and Halloysite. These have two layered structure that is called the T-O structure (meaning tetrahedral octahedral structure), without any charge imbalance. They are stable as such. The differently layers of this material are bonded by Vander Waals forces (which are weak forces).  
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**Main Classes of Clays**

Smectites such as Pyrophyllite and Montmorillinite have three - layer structures (T-O-T), with some charge imbalance.


*These clays readily adsorb water between the layers, which generally reduces the strength and causes swelling.*

Pyrophyllite  $Al_2Si_4O_{10}(OH)_2$

○ O  
 ● OH  
 ○ Mg<sup>2+</sup>  
 ● Al<sup>3+</sup>  
 ● Si<sup>4+</sup>

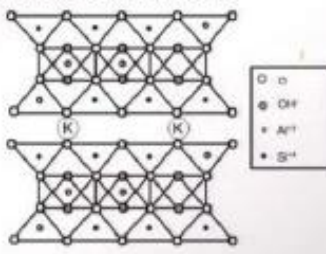
We have another class of clays called Smectite (which includes Pyrophyllite and Montmorillinite), which has a three layered structure called the T-O-T structure (tetrahedral octahedral tetrahedral structure) and having some charge imbalance. So, there is some charge imbalance in the structure and this makes it such that water is readily adsorbed between the layers and once water goes in, it leads to swelling of the clay. Strength of the bond between the different layers is lost which makes these clay layers separate very easily. This is in case of smectites.

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 **Main Classes of Clays**

Illites like Muscovite are three-layered (T-O-T) with K, Ca, or Mg interlayer cations, which prevent the entrance of water into the structure. Therefore, these clays are non-expanding.

Muscovite  $KAl_2AlSi_2O_{10}(OH)_2$




The diagram illustrates the Muscovite crystal structure, which is a three-layered (T-O-T) structure. It shows two tetrahedral sheets (T) sandwiching an octahedral sheet (O). The tetrahedral sheets are composed of silicon (Si<sup>4+</sup>) and aluminum (Al<sup>3+</sup>) ions, while the octahedral sheet is composed of aluminum (Al<sup>3+</sup>) and hydroxyl (OH<sup>-</sup>) ions. Potassium (K<sup>+</sup>) cations are located between the layers to balance the charge. A legend indicates the symbols used: a circle for Oxygen (O), a square for Hydroxyl (OH), a triangle for Aluminum (Al<sup>3+</sup>), and a diamond for Silicon (Si<sup>4+</sup>).

Then we have a third class of clay called Illites. Muscovite is one of them which also has a three layered T-O-T structure, but with Potassium, Calcium or Magnesium cations between the layers. Here you see the T-O-T structure of muscovite with potassium cations between the sheets. These potassium ions now fulfill the charge imbalance. They do not let any water go in. So, this is a type of clay which does not incorporate water and expand. This is non-expanding clay, even though it has similar structure to that of Smectite.

So, what we have seen is you can have a similar structure, but depending on the chemical nature of these structures, they can be either expanding or non-expanding. That is important for us to understand when we look at foundations and soil mechanics, and we want to build structures on such soils.

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 **Features of Flat Sheet Structures**

- Clay crystallises as flat plates that cleave easily along the weakly bonded plane.
- Similarly, mica can be cleaved into very thin sheets.
- Dry clay (and talc) has a slippery feel due to the plates sliding across one another.

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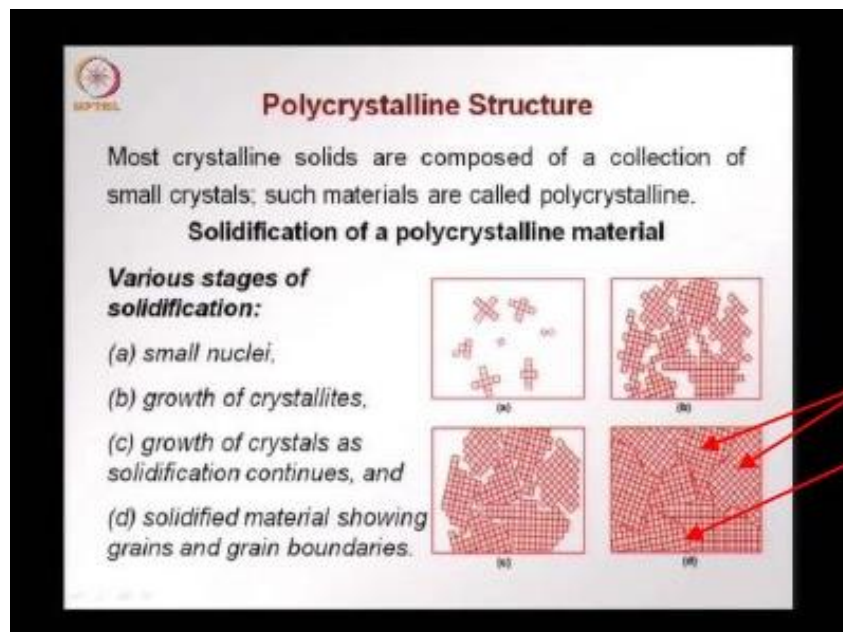
We summarize about clays. Clays crystallize as flat plates that can cleave easily. That means they can separate easily along the weakly bonded planes. What are the weakly bonded planes? They are those that are bonded by Vander Waals bonds. Other bonds like ionic, that we saw before, do not break so easily. But the Vander Waals bond breaks easily and the plates of clay can separate.

Similarly, we also seen in mica which can also be separated into very thin sheet or cleaved into very thin sheets.

One evidence for these plates separating easily is that when you take dry clay and rub it with your finger, you get a slippery feel. Same with talc or talcum powder.

The platelets of clay slip over each other and that is why, when you take clay powder in between your fingers, you get a slipper feel.

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Crystal

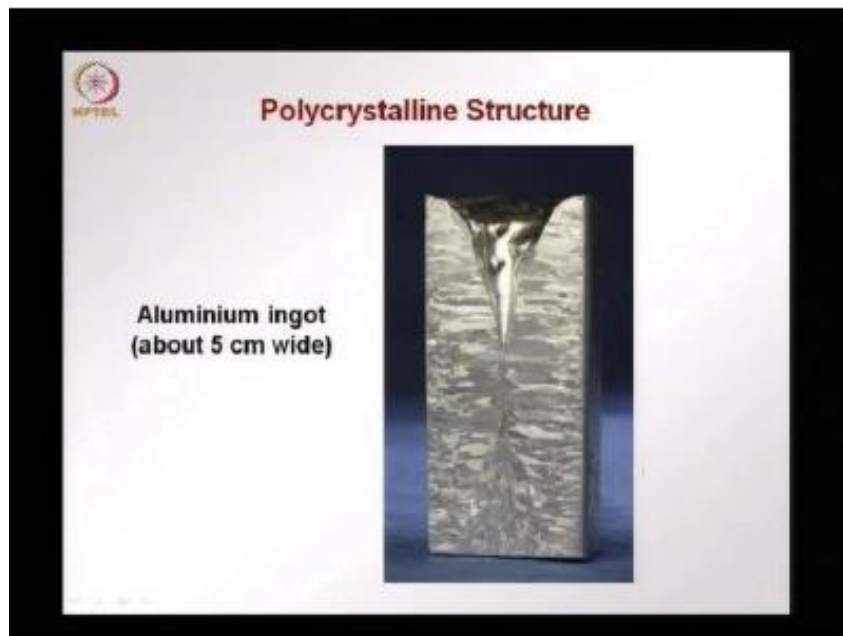
Grain boundary

Now when we have materials, generally they are polycrystalline. The whole solid is not made up of a single crystal but a collection of small crystals and therefore, they are called polycrystalline materials. The different stages of solidification are shown. When we have a melt and we start decreasing the temperature of the melt, small nuclei start to solidify and around these nuclei, we see the growth of the crystal. So here, we are seeing the evidence for some sort of growth around the different nuclei.

As the solidification continues, each nuclei grows into a large crystal and this grows without any

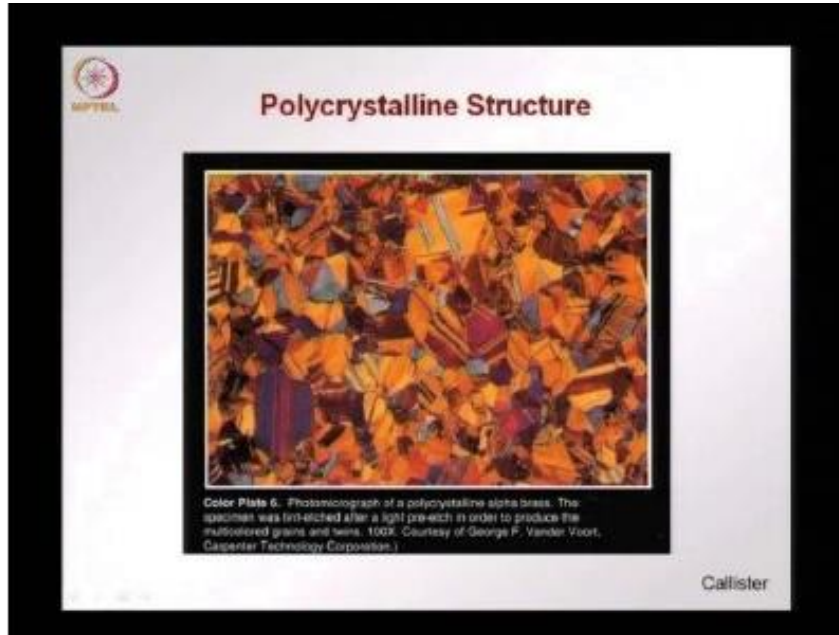
hindrance/disturbance until one crystal meets another. So when one crystal hits another or does not have space to grow, we have a grain boundary. Within a grain the crystal structure is in a certain direction. The next crystal can have a different crystal direction or orientation. Eventually all the spaces filled up and what you have these grain boundaries, that you see between the different crystals. So, each of this will be one crystal and between the crystals, we have grain boundary.

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This is an example of the grain boundaries and different crystals. This is an image, from the internet, of an aluminum ingot about five cm wide, as it is solidified. You can see that all of it is aluminum, but the different colors indicate the different crystals that have been formed. This is an ingot which would have solidified first along the edges and then you have radial solidification. So, you have these elongated crystals which are formed and finally, there is crystallization or solidification at the centre. So, these different colors indicate different crystals that have been formed.

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Now this is an image from the book of Callister, showing micrograph of brass and its poly crystalline nature. Again all this is brass and the different colors represent the different crystals which reflect light differently because of different orientation of the crystal planes. And you see here how brass is made of different crystals or grains and between them we have the grain boundary. So, within one grain, the crystal structure is uniform and between one grain and other you will have a discontinuity of the crystal structure.

To summarize, in the first part of this lecture we looked at different crystalline structures formed by either ionic, metallic or covalent bonding. We also looked at what properties can be expected from such structures and we ended up looking at poly crystalline materials. In the next part of this lecture, we will look at the defects that can occur in these crystals. Remember, we said crystals are materials which have orderly packing or regular structure. Now defects can also occur in these materials and this is what we will look at when we continue with this lecture and later on we will look at structures which are not crystalline; they are either precipitates or are glasses. So, these are called amorphous structures which can form. The amorphous structure, by definition, is an irregular structure that can form in materials.

Thank you.