An Introduction to Materials: Nature and Properties
(Part 1: Structure of Materials)

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Lecture – 14

Structure of Metals and Alloys

So, now we start next lecture which is lecture 14 on which is now. So, now, we have learnt about the crystallography we have seen the miller indices. Now, we will see how atoms pack in a given structure and give rise to various structures in solids. So, in this series the first material system that we consider is of metals and alloys and we will see that how atoms pack in metals to give rise to various structures and what can we learn from that.

So, the issues that we will address are one.

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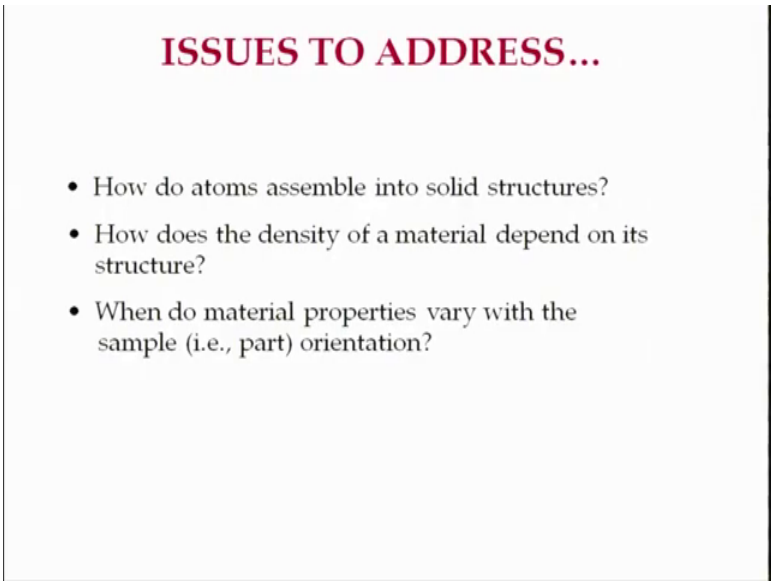

ISSUES TO ADDRESS...

- How do atoms assemble into solid structures?
- How does the density of a material depend on its structure?
- When do material properties vary with the sample (i.e., part) orientation?

How do atoms assemble in solid structures? How does the density of a material depend upon it is structure? And when do material properties vary with the for example, a sample orientation? I do not know whether we can be able to do this particular part or not but we will try and do the first.

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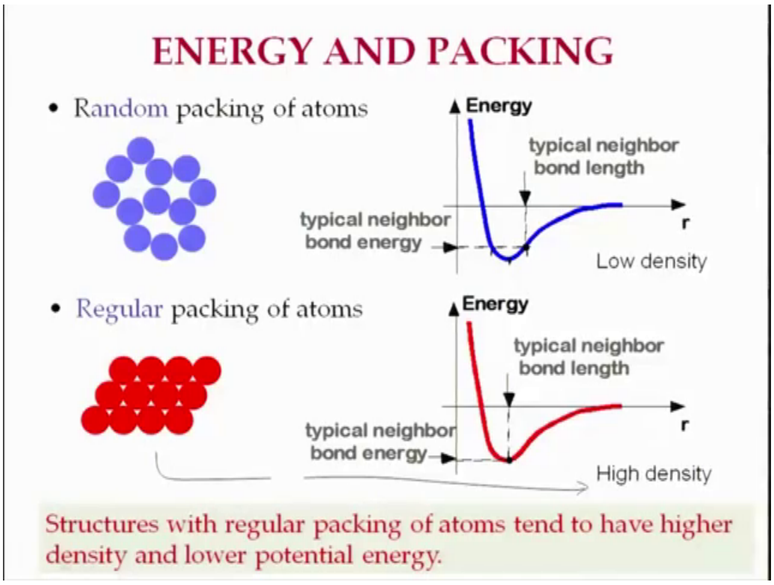

ENERGY AND PACKING

- Random packing of atoms
- Regular packing of atoms

Structures with regular packing of atoms tend to have higher density and lower potential energy.

The first two maybe we will take up some of these in the next lecture. So, the first thing that we consider is the energy energetics and packing, packing of atoms with respect to energy of the and symbols. So, random in if you have random packing of atoms where atoms do not particular follow a configuration they are random with respect to each other. So, the neighborhood of each of the atoms is different some packed some areas are dense some areas are lose. So, as a result you have you can draw the energy versus distance configuration.

These systems as you can see these are typically low energy low density system, low density system and they have lower bond energy as compared to. So, you are not here which is the equilibrium separation between the atoms you are somewhere here which is the you cannot be here, you cannot be here because you are in a very strongly lower distance is not possible because there will be strong repulsion between the atoms you will immediately get into this region this region is very steep.

So, typically lower separation is not possible, but higher separation is possible. So, you are in somewhere, somewhere in this region. So, the overall energy of the system potential energy or the bond energy lower. So, as a result you are not at the free energy minima, but you are at slightly higher energy so, which has which whose deprecation is lower bond energy in this system.

On the other hand you have systems in which atoms regularly packed themselves. So, you have configurations like this in which atoms are arranged in such a fashion that they touch each other. So, I mean physically physics vise is speaking then they can never touch each other, but they are in close proximity to each other determined by the energy landscape and here the energy corresponding to this configuration is minimum.

So, as a result they tend to have higher bond energy and they tend to have higher density. So, their density of systems in which atoms regularly pack themselves which have a periodicity and same the same kind configuration of each atom around each other each atom within the lattice. So, this atom whether you will look at this atom or this atom or this atom all of them have same neighborhood.

So, in such systems they have higher bond energy there they have better stability and they have high density. So, regular packing of atoms leads to high density so that is why metals typically tend to have higher density because atoms are regularly packed in them. On the other hand if you look at glasses for example, glasses or amorphous solids, solids in which atoms are not regularly packed in this kind of they are present in this kind of fashion there their density tends to be lower. So, we can summarize that structures with regular packing of atoms tend to have higher density and lower potential energy or higher bond energy.

So, this is the outline of this particular see topic.

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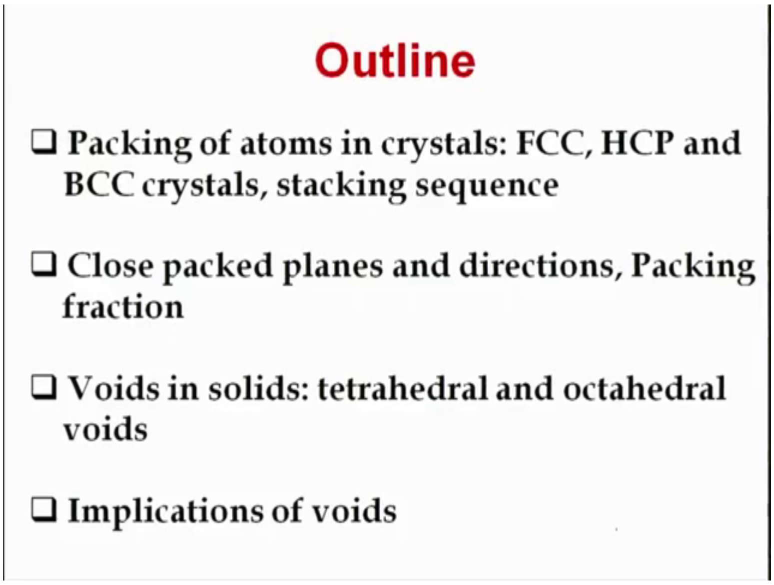

Outline

- ☐ Packing of atoms in crystals: FCC, HCP and BCC crystals, stacking sequence
- ☐ Close packed planes and directions, Packing fraction
- ☐ Voids in solids: tetrahedral and octahedral voids
- ☐ Implications of voids

So, we will see about the packing of atoms and crystals the close packed planes and directions packing fraction voids in solids perhaps not possible in this lecture, but maybe in this or in next lecture an implication of these voids, what do we mean by these voids? What is the importance of these voids in solids in metallic solids?

So, there are two, based on the above classification.

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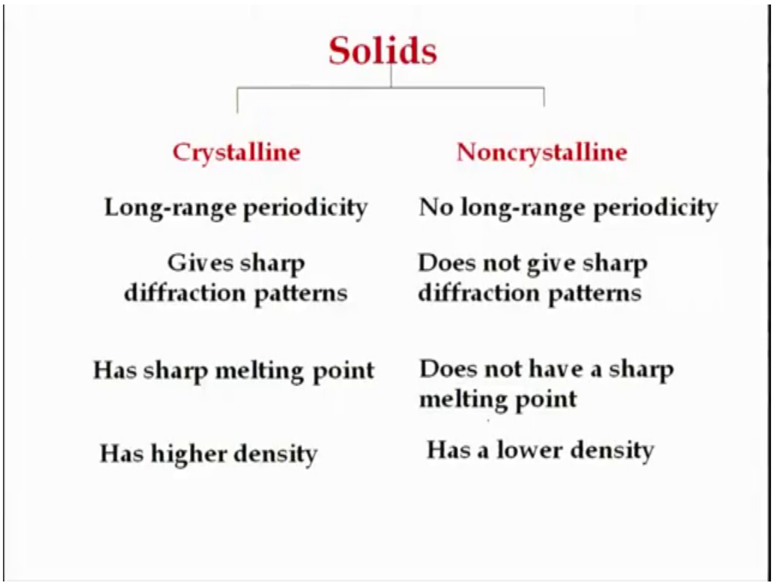

Solids

Crystalline	Noncrystalline
Long-range periodicity	No long-range periodicity
Gives sharp diffraction patterns	Does not give sharp diffraction patterns
Has sharp melting point	Does not have a sharp melting point
Has higher density	Has a lower density

Which I was gave you in the previous slide there are two kinds of solids, one is crystalline second is non crystalline. Crystalline solids have long range periodicity as we will see later on they give very sharp diffraction pattern.

So, one way to examine crystalline materials is to use the diffraction x ray diffraction electron diffraction and they give very sharp diffraction patterns because of periodicity you know from your twelfth standard physics that atoms can be the regular array of atoms can be considered as if it is a regular slits slit pattern and you know Thomas young's experiment when the light or a or a wave meets a regular array of slits it undergoes diffraction. So, and diffraction can be noted on a screen or on a detector.

So, crystalline solids with regular arrangement of atoms give very sharp diffraction patterns they have very they have a typical melting point, melting point is well defined sharp melting points mean means well defined melting point. So, for example, aluminum has a melting point of 667 degree centigrade it is a well defined melting point copper has a melting point of 1083 degree centigrade it is well defined melting point and they have a crystalline solid typically has higher density. So, all of them they have variations within them, but since atoms are closely packed they are touching each other and the solids are fairly well packed they have high density.

On the other hand non crystalline solids they do not have long range periodicity. So, examples are amorphous materials or glasses or polymers even many polymers they do not have long range periodicity which means the periodicity of atoms do not go beyond let us say few tens of nanometers it is just few nano meters and after that it is different periodicity. So, they do not have long range periodicity of particular kind as a result if you examine them using X-ray diffraction they do not give very sharp diffraction patterns.

So, this is one distinction between crystalline and non crystalline materials when you take the x ray diffraction pattern in this case you will see very sharp pattern in this case you will see very in the crystalline case you will see very sharp pattern and the non crystalline say material you will get very diffused pattern. Non crystalline materials also do not have very sharp melting point we will see that later on.

So, this is another distinction between them so, when you do thermal analysis to find out the melting point you will see that there is no very sharp peak in the thermal analysis and as a result they have very low they have lower density as compared to crystalline materials. So, polymers typically are lighter and not only because they use they have elements which are lighter, but they also have a period non periodic structures which result in even lower density.

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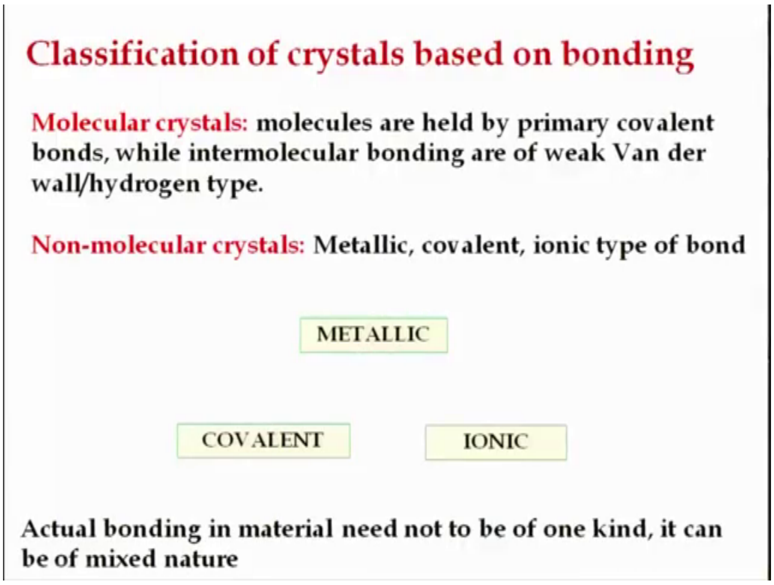

Classification of crystals based on bonding

Molecular crystals: molecules are held by primary covalent bonds, while intermolecular bonding are of weak Van der wall/hydrogen type.

Non-molecular crystals: Metallic, covalent, ionic type of bond

METALLIC

COVALENT

IONIC

Actual bonding in material need not to be of one kind, it can be of mixed nature

So, based on you can another you can do another classification based on bonding the crystals in which molecules are held together by primary covalent bonds whereas, intra molecular bonding could be of weak Van der Waals type or hydrogen type these are molecular crystals such as polymers non molecular crystals are held together in these crystals atoms are held together by metallic or covalent or ionic type of bond predominantly.

So, that is why this is these are the three classes that you can have metallic covalent and ionic. Actual bonding may not be completely metallic or completely covalent or completely ionic that may be a mix of them, but it is normally dominated by one type of bonding and there are no secondary bonds present there.

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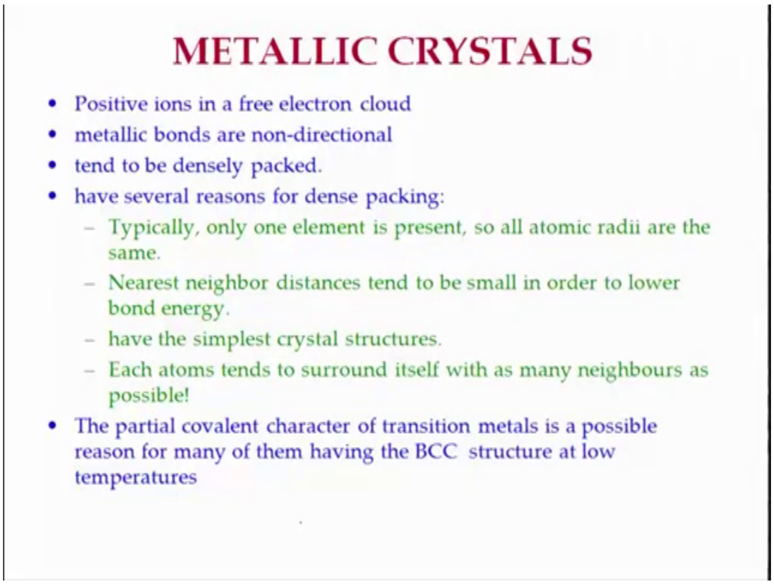

METALLIC CRYSTALS

- Positive ions in a free electron cloud
- metallic bonds are non-directional
- tend to be densely packed.
- have several reasons for dense packing:
  - Typically, only one element is present, so all atomic radii are the same.
  - Nearest neighbor distances tend to be small in order to lower bond energy.
  - have the simplest crystal structures.
  - Each atoms tends to surround itself with as many neighbours as possible!
- The partial covalent character of transition metals is a possible reason for many of them having the BCC structure at low temperatures

So, metallic crystals can be defined you know that they have positive ions and positive ions core is surrounded by a free electron cloud, metallic bonds tend to be non directional in nature in case of covalency because electrons are located in certain orbitals and orbitals have a particular shape of them it is the way strong directionality with the covalent bonds, but metallic bonds do not have a directionality.

They tend to be densely packed metallic crystals and they have several reasons for dense packing one, typically only one element is present as a result all the atoms have same radius. So, that also that allows for so, if you have multiple radius is present then there may be confusion which one to choose as a neighbor. So, as a result there may be a lack of order. But since you have only one type of element present by enlarge they undergo dense packing.

As a result the nearest neighbor distances tend to be smaller and smaller, nearer and nearest neighbor distances lower the bond energy bond energy and they have simple crystal structures and each atoms tend to surround itself with as many neighbors as possible. So, these two are correlated and then in some cases some metals are partially covalent and that is why some of them have BCC structure for example, at low temperatures and we will see that, what is the implication in terms of BCC, FCC structures in the coming slides.

We will see that BCC structure is has low lower packing density as compared to for example, FCC structure. So, although we are saying that they tend to be densely packed at some of the materials are not so densely packed as compared to others and there are reasons in terms of bonding.

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Metallic Crystals

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

So, metallic crystals typically you can divide them in 3 structures by enlarge, FCC structured metals are aluminum iron between 910 to 1410 degree centigrade copper silver, gold, nickel, palladium, platinum all of these are FCC structured materials, Face Centered Cubic FCC means Face Centered Cubic. Body Centered Cubic materials are lithium, potassium, sodium, titanium, zirconium, hafnium, niobium, tantalum, chromium, molybdenum, Tungsten, iron at room temperature below 910 Kelvin up to room temperature is even below it is 910 Kelvin be below room temperature it is BCC and then there are some metals which are HCP hexagonal close packed.

We have talked about hexagonal system hexagonal lattice, but we are not talked about hexagonal close packed we will see what hexagonal close packed system is metals like beryllium, magnesium, titanium, zirconium, hafnium, zinc, cadmium they all are hexagonal close packed structured materials. So, let us first look at the structure of material metals by packing of spheres in the space.

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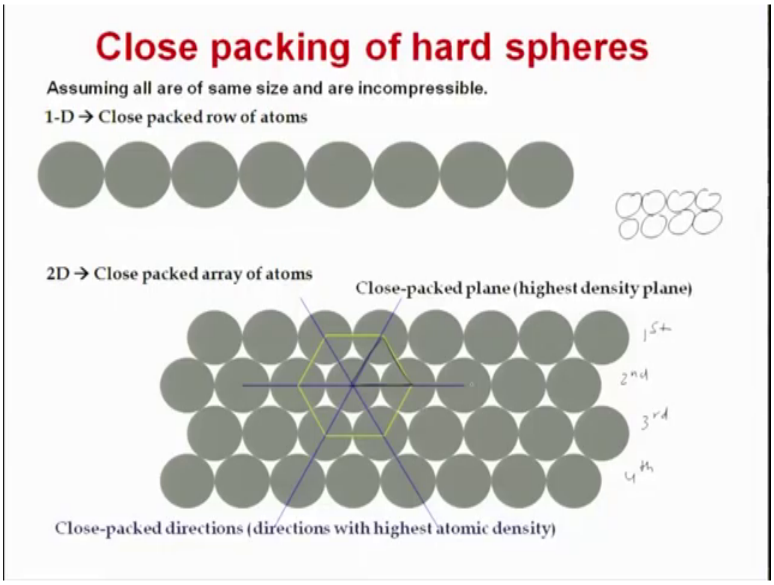

Close packing of hard spheres

Assuming all are of same size and are incompressible.

1-D → Close packed row of atoms

2D → Close packed array of atoms

Close-packed plane (highest density plane)

Close-packed directions (directions with highest atomic density)

So, assuming all the spheres are hard they are incompressible they are of same size. So, in 1 D you can have this kind of configuration you can have a close packed row of atoms. So, this all the atoms are packed in such a fashion. So, they are next to each other along a row.

In the 2 D case the close packed array may be something like that. So, this is the first row, this is the second row. So, this is first, second, third and fourth row. So, you have the first the second row goes into the position which is the minimum energy position where it finds highest number of neighbors with respect to each other if it goes in this position it could have gone in this position.

So, you have the first row and then you have the second row like this, a difference is in this case the number of neighbors is lower, but in this case the number of neighbors is higher on this side you have only one neighbor on this side, you have one neighbor on this side, you will have one neighbor and on the other side you will have one neighbor.

In this case you have one neighbor on 2 neighbors on top, 2 neighbors within the row and 2 neighbors at the bottom. So, you have 6 neighbors so, this is called as a close packed plane the highest possible highest density plane. So, this is how if the atoms are spherical in nature this is the highest atomic density that you can find within a 2 D plane. This will be the sort of representation of a plane it is a hexagonal shaped plane you can also say it is a triangle, equilateral triangle if you can draw a equilateral triangle here, but you generally do not use triangle as a representation in matters and you have closed packed directions the directions now the depicted those depicted in blue are the directions with a highest atomic density.

So, this direction, that direction, this direction they are all so, how many directions are there within planes which are close packed?

Student: 2 by 3

You have 3 directions and if you take the negative indices around this is 6 directions 6 direction within a plane which are close packed, but you have 3 rows of atoms with 3 distinct rows of atoms which are close packed and which are at equal angles to each other.

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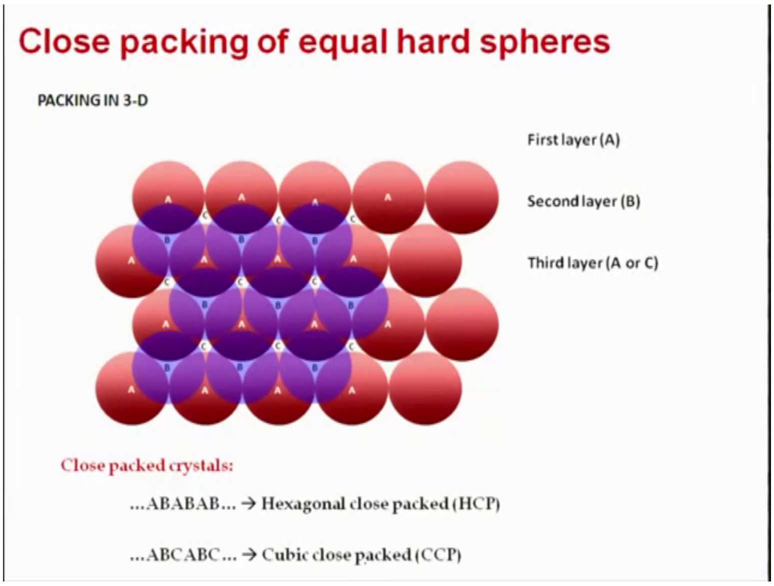

Close packing of equal hard spheres

PACKING IN 3-D

First layer (A)

Second layer (B)

Third layer (A or C)

Close packed crystals:

...ABABAB... → Hexagonal close packed (HCP)

...ABCABC... → Cubic close packed (CCP)

So, if you look at the close packing of equal sized hard spheres packing in 3 D and this is the first layer which I depict by A, then I have a second layer which can go here or here on top of B or on top of C. So, let us say I managed to put them on top of B; third layer can go either on top of A.

Student: (Refer Time: 15:33).

Or on top of C so, if it is AB AB AB then what it makes is a hexagonal close packed structure and if it is a ABC ABC ABC it will make a cubic close packed structure which turns out to be face centered cubic lattice. So, this is how you will have packing.

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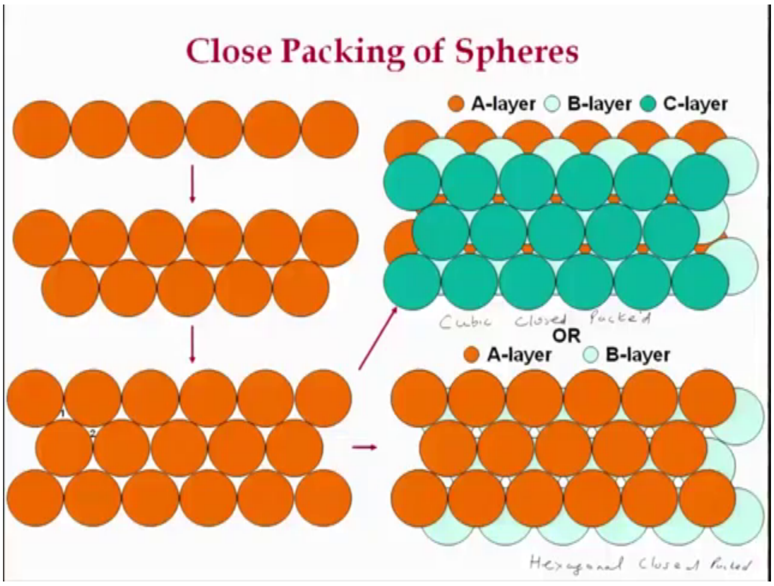

Close Packing of Spheres

First row, second row, third row then you put another layer on top, you put another layer on top this is the AB or first layer, second layer, third layer this is.

Student: ABC ABC.

ABC ABC kind of packing so, this one is as we will see it will be hexagonal close packed you have not seen it yet I am just telling you what it is and this is this will be cubic we will see how right now you do not have any information on how it is just a word a mouth.

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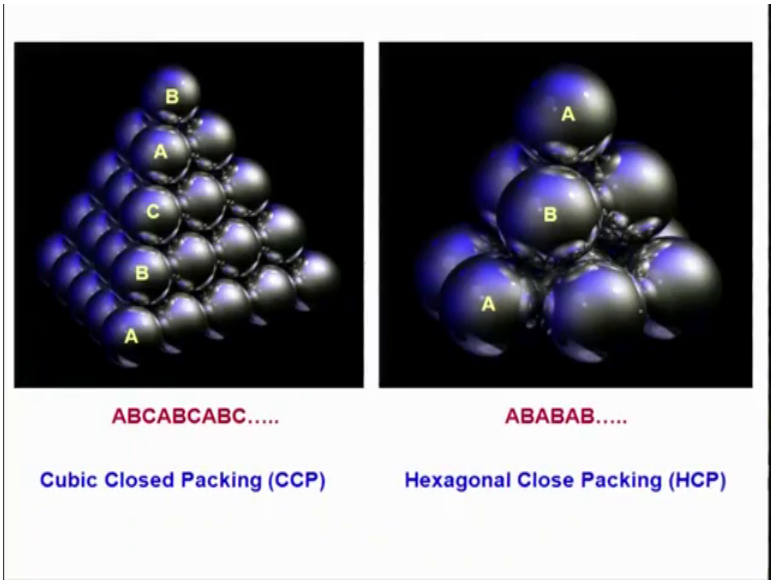

ABCABCABC…..

Cubic Closed Packing (CCP)

ABABAB…..

Hexagonal Close Packing (HCP)

So, this is how the packing will look like in 3 D the first layer, the second layer, the third layer and then the next layer which will again be A layer third, then the next layer which will again be B layer and C layer and so on and so forth.

In this case A layer, B layer and then A layer you can do this experiment by buying pebbles or small metallic spheres which are put in cycles just make a grid of those atoms those metal balls and try arranging them with respect to each other and you can see that 2 different structures can be made.

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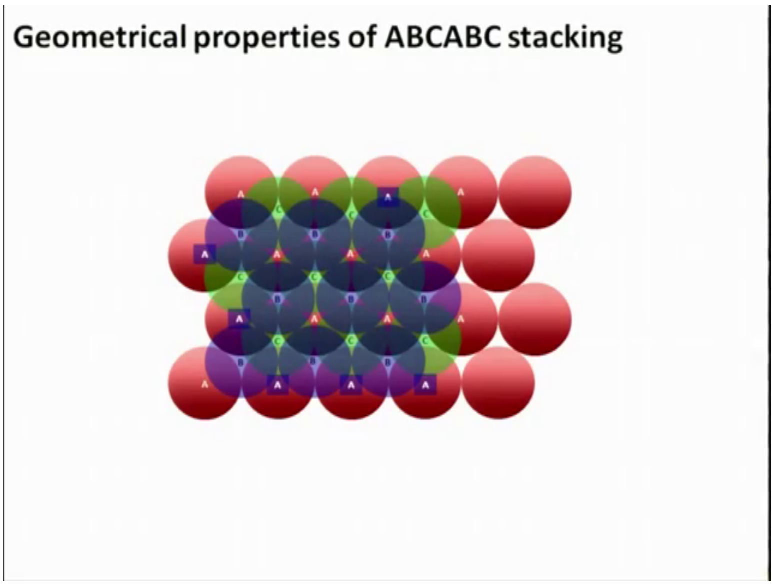

Geometrical properties of ABCABC stacking

So, this is A and B and C.

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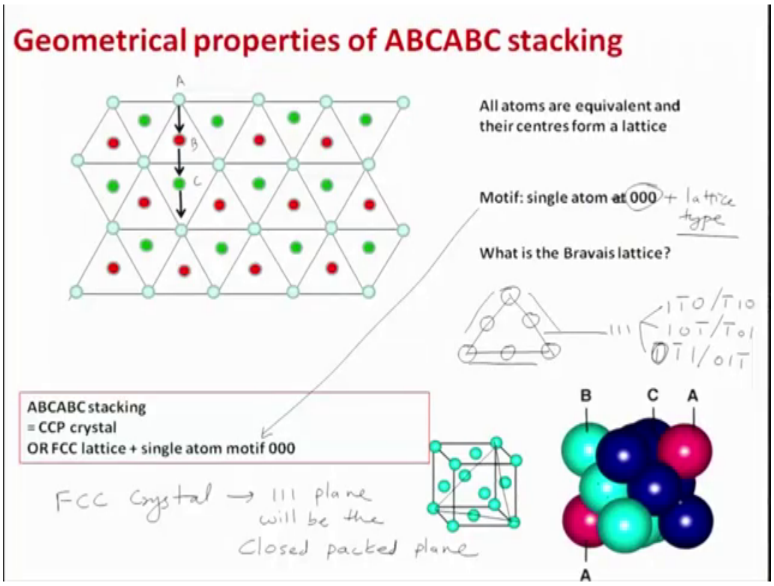

Geometrical properties of ABCABC stacking

All atoms are equivalent and their centres form a lattice

Motif: single atom ~~at~~ 000 + lattice type

What is the Bravais lattice?

111 $1\bar{1}0/\bar{1}10$, $10\bar{1}/\bar{1}01$, $0\bar{1}1/01\bar{1}$

ABCABC stacking
= CCP crystal
OR FCC lattice + single atom motif 000

FCC Crystal → 111 plane will be the Closed packed plane

And geometrically it looks something like this you have if you connect these this one lies in the bottom layer. So, this is A, this was B and this was C all of these atoms are equivalent, I have chosen this to be A, this to be B and this to be C, but I could have very well chosen this as A, this as B and then A which will come on top of C will become C.

So, in that sense all the atoms are equivalent and their centers form a lattice. So, basically what you have is the motif is a single atom at 000, what is the Bravais lattice? Bravais lattice if you have ABC ABC stacking, it makes a cubic close packed crystal. If you have motif at single atom, then you need to describe what is the lattice type? Without that because so we need to find out what is the lattice type because without that it is a incomplete.

So, the structure which will look like is in the ABC ABC packing it is called as cubic close pack crystal or a FCC lattice with single atom motif at 000. So, this is the answer here motif is at 000 single atom, but what is the Bravais lattice, Bravais lattice is the FCC at 0 0 plus FCC lattice will automatically mean you have 4 lattice points one at 000, another one at half half 0, another one at half 0 half and another one at 0 half half.

It is you can form within this unit cell you can form a structure which looks like this, this is. So, you can see that this is the A layer, this is the B layer, this is the A layer, this is B layer, this is C layer, this is A layer and within this you can form a cube and the cube interestingly. So, this looks like a hexagonal pattern right, but I am saying that you are forming a cubic crystal and this is because the atoms are arranged in such a fashion if you now consider a cube. So, this is the cube right within this cube if I connect the corners of cube with the let us say if I connect what is the arrangement of atoms along this particular plane this is a 1 1 type of plane right.

If you remember 1 1 1 type of plane had a arrangement like this, this and if I make it bigger in 2 D it will be a hexagonal type of arrangement. So, basically all these atoms which are shown here ABC pattern they are nothing, but 1 1 1 plane stacked on top of each other. So, here this is the one, this is one of the atoms of that 1 1 1 plane these are the few other atoms of that B 1 1 1 type of plane which is the B layer, this is again the C layer of 1 1 1 type of plane and then again you have 1 1 1 type of plane of A layer.

So, within this you can construct a lattice which is called as a cubic close packed lattice and these atoms are arranged in this plane on 1 1 1 plane so, 1 1 1 plane in a FCC lattice. So, FCC crystal 1 1 1 plane will be the close packed plane and you can see what are these directions now which are the close packed directions, these are the close packed directions right what are the what is the indices of these directions, these directions are if a direction lies within a plane then the dot product should be equal to 0.

So, if this plane is 1 1 1 then the direction will be 1 bar 1 0, 1 0 bar 1 or 0 bar 1 1 you can write this as bar 1 1 0 can write this as bar 0 1 and you can write this as 0 1 1 bar. So, these directions which you see on the face they are the close packed directions and the plane that you formed within the unit cell is the close packed plane that 1 1 1 plane.

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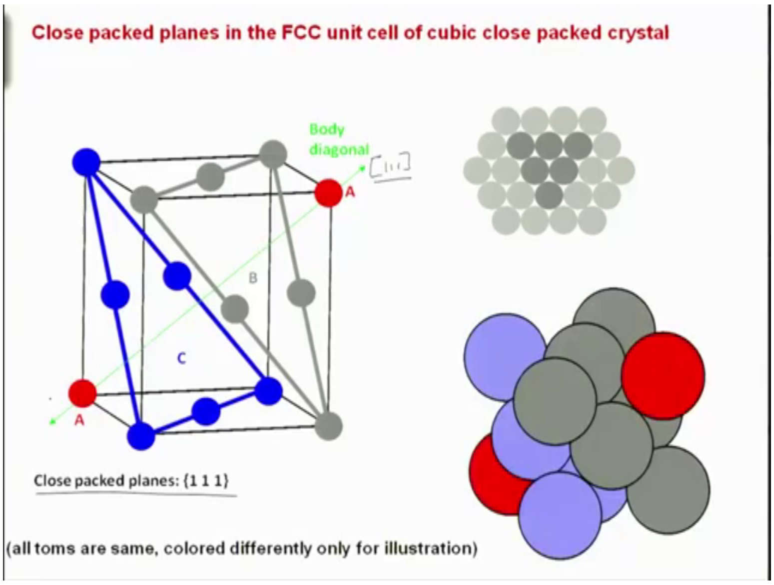

Close packed planes in the FCC unit cell of cubic close packed crystal

Close packed planes: {1 1 1}

(all toms are same, colored differently only for illustration)

So, this is the FCC unit cell so, this is the close packed plane, these are the close packed planes, this is the direction, this is, this is not the closed pack direction, this is just a body diagonal body diagonal is perpendicular to these planes body diagonal is nothing, but 1 1 1 type and for a cube we know that this is perpendicular to 1 1 1 plane.

So, all the close packed planes are of 1 1 1 type in this case I have drawn the atoms in different color, but they are of different, they are of same color for different color is drawn only for illustration. So, that you can so, see two different planes. So, this is A layer, this is B layer, this is C layer, than the again A layer all right this is what you form as a FCC structure.

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Stacking sequence?

So, this is the stacking sequence you can say it is set of oranges or, a set of ladoos sort of.

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Stacking sequence?

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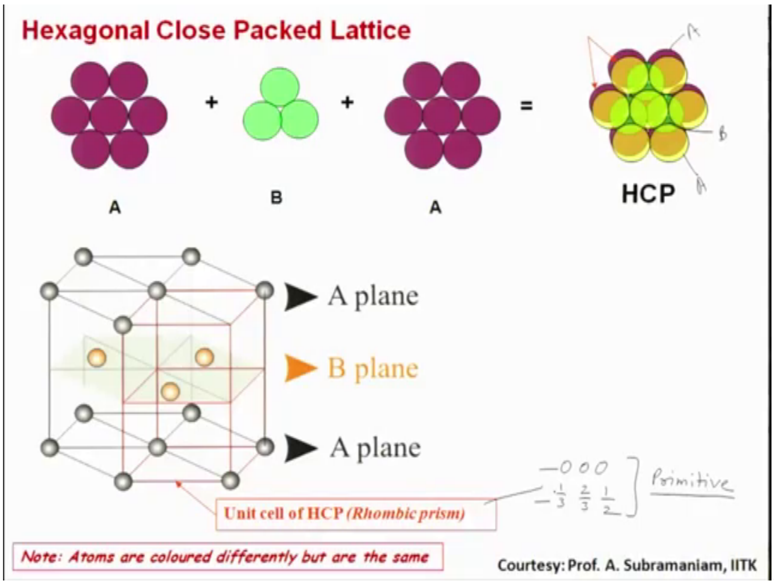

Hexagonal Close Packed Lattice

Unit cell of HCP *(Rhombic prism)*

Note: Atoms are coloured differently but are the same

Courtesy: Prof. A. Subramaniam, IITK

Now, let us look at the hexagonal arrangement. So, hexagonal arrangement is you have these 6 atoms in the A layer, then again B layer I have chosen only 3 atoms, but the B layer can be continuous beyond the 3 atoms and then again A layer. So, this kind of stacking will give me the bottom layer which is the purple color, the intermediate green layer, the top layer which I have now converted as a yellow, but it is a same layer.

So, this is sorry. So, this is my A layer these are B layers and these this is again A layer basically on top of each other crystallographically you will see this see it like this you have A plane, you have B plane and you have A plane again.

So, this is basically the hexagonal closed packed crystal unit cell and the one unit cell that you see is the smaller one which is a red one which is called as rhombic prism. So, it has atoms at, in this case there will be one atom at 0 0 0, another atom at 1 by 3 2 by 3 half and this is a primitive lattice, primitive lattice with motif being a combination of these 2 atoms motif being combination of atom here and combination of atom here.

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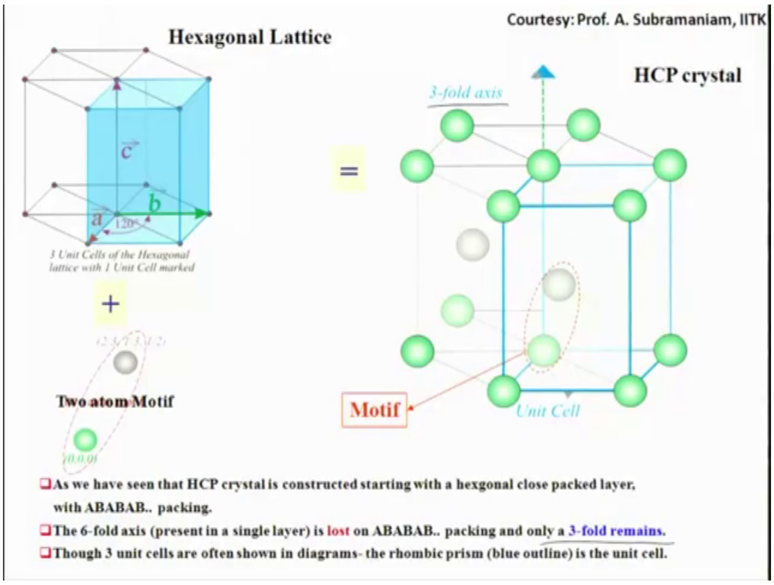

Courtesy: Prof. A. Subramaniam, IITK

- As we have seen that HCP crystal is constructed starting with a hexgonal close packed layer, with ABABAB.. packing.
- The 6-fold axis (present in a single layer) is lost on ABABAB.. packing and only a 3-fold remains.
- Though 3 unit cells are often shown in diagrams- the rhombic prism (blue outline) is the unit cell.

So, this is basically the hexagonal unit cell they are smaller lattice ABC axis the same orientation 120 degree between A and B and the motif is combination of these 2 and if you rotate it has a threefold symmetry and the motif 2 atom motif one lies at 0 0 0, another lies at 2 by 3 1 by 3 half or it you can write it as 1 by 3 2 by 3 half depending upon the way you look at it and because of present of presence of intermediate layer, that is B layer in the in one single layer if you have just one single layer the top layer let us say you have a 6 fold right you can rotate it by 60 degree and you still achieve the same configuration.

But because of presence of this B layer now you have lost that 6 fold. So, what you now have is just a threefold access. So, only a 3 fold remains in this lattice and although I have shown the 3 unit cells here the unit cell actually is the smaller one which is the smaller unit cell which is a rhombic prism w 1.

Student: (Refer Time: 26:54) is the primitive unit cell.

This is the primitive unit cell because both of them are needed to define the unit cell. So, if you go I mean. So, these are not two different lattice points then the sorry they are not the same lattice points there they are the there are different lattice points.

Student: They are (Refer Time: 27:14) associated (Refer Time: 27:15).

Yeah. So, you can choose the you can put the corner of the lattice between two of them it is like a dumbbell shaped kind of thing.

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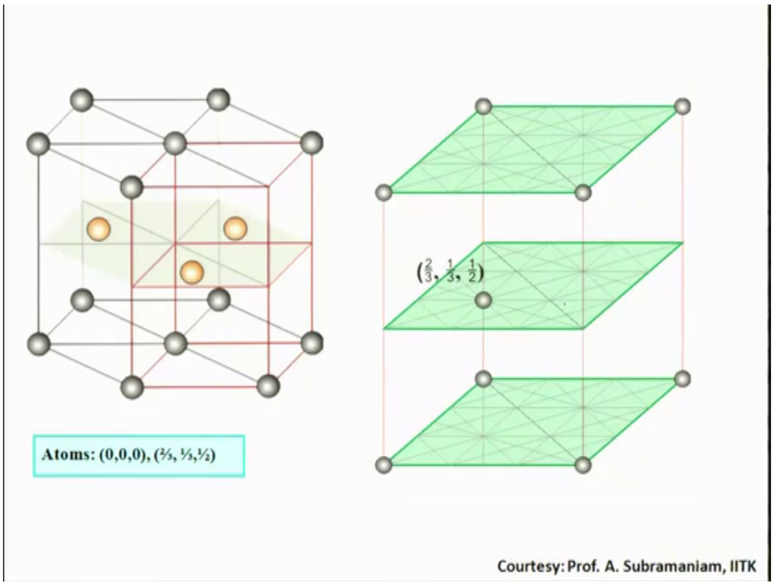

Atoms: (0,0,0), (⅔,⅓,½)

Courtesy: Prof. A. Subramaniam, IITK

So, this is that another representation of a hexagonal unit hexagonal closed pack lattice.

So, let us see the geometrical properties.

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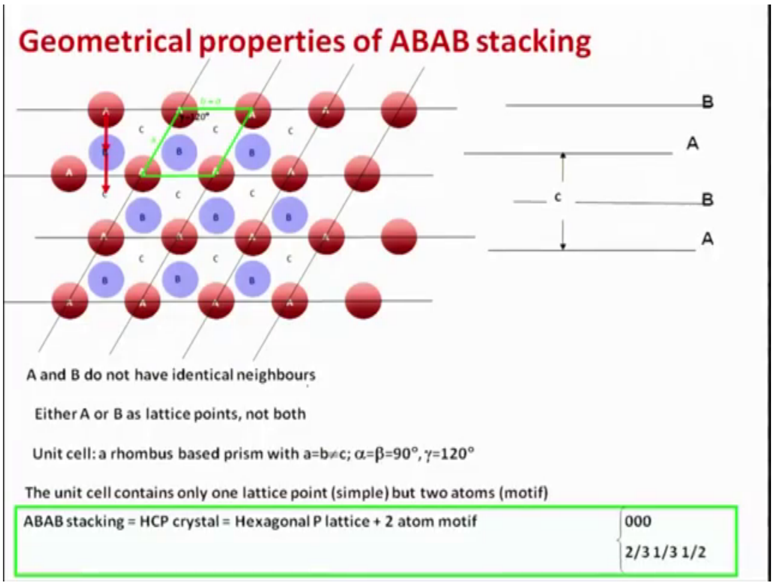


Geometrical properties of ABAB stacking

A and B do not have identical neighbours

Either A or B as lattice points, not both

Unit cell: a rhombus based prism with $a=b\neq c$; $\alpha=\beta=90°$, $\gamma=120°$

The unit cell contains only one lattice point (simple) but two atoms (motif)

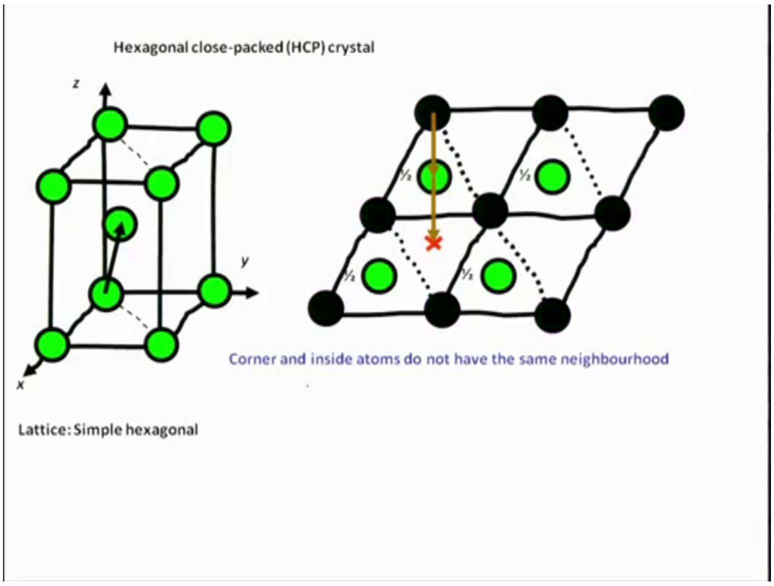
ABAB stacking = HCP crystal = Hexagonal P lattice + 2 atom motif
000
2/3 1/3 1/2

In this case you have ABAB kind of stacking I have just made them a little smaller. So, here the reason why these are, why it is a primitive unit cell because A and B do not have identical orientation of neighbors you see the definition was that each lattice point must be if it is same then it must have identical neighborhood, here they do not have a identical neighborhood because of this presence of vacant let us say C position or there is no C position, as such as a result you need to come as a result you need to compare combine both of them to have identical neighborhood.

So, that so if you remember the discussion that we have during primitive non primitive lattices you need to combine both of them to call it as a proper lattice. So, that is why so A and B do not have identical neighbors as either A or B as lattice points, but not both. So, that is why you need a unit cell contains only one lattice point, but 2 atoms, you do not consider both of them as different lattice points.

So, this is the hexagonal close packed structure.

(Refer Slide Time: 29:05)



Hexagonal close-packed (HCP) crystal

Corner and inside atoms do not have the same neighbourhood

Lattice: Simple hexagonal

So, we will close this lecture here in the next class we will look at some other variations on metallic solids like BCC simple cubic and we look at other properties like packing fractions inter stresses voids any questions.

Student: Sir (Refer Time: 29:27).