Lecture 8
Tu 12.08.2025
Thursday Group
meets on sep 11
for Exp 3 on XRD

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Lecture 8

Allotropy
Graphene: Lattice and Motif
Fullerene
Nanotube: Armchair, zigzag and chiral

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Structure of Solids

Raghavan Ch 5

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1. Crystalline structure of Elements

2. Crystalline structure of Compounds and 'solid solutions'

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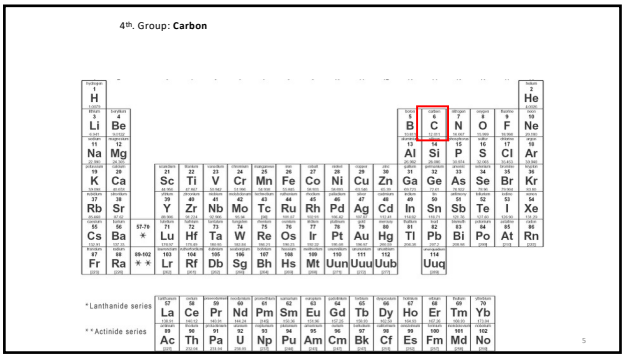

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Allotropy

The phenomenon of the same element in the same state (solid/liquid/gas) occurring in different structural forms.

Fe Monatomic BCC at Room Temperature (Ferrite)

Fe Cubic Close-Packed (CCP), Bravais lattice: FCC, Austenite Above 910 C

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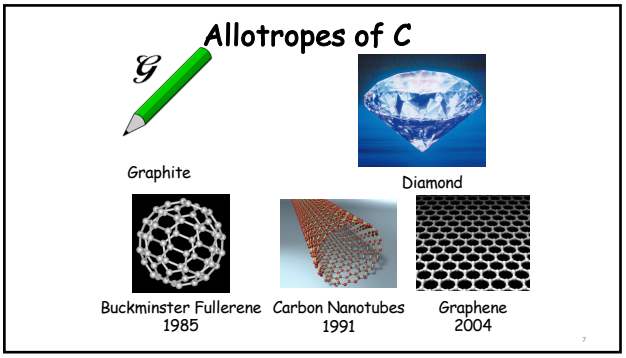

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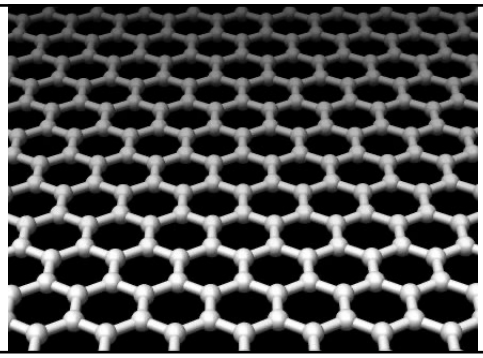

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Structure of Graphene

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3. Motif

Relation between crystal and lattice?

Crystal = Lattice + Motif

Motif or basis: an atom or a group of atoms associated with each lattice point

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Crystal = Lattice + Motif

How to repeat

What to repeat

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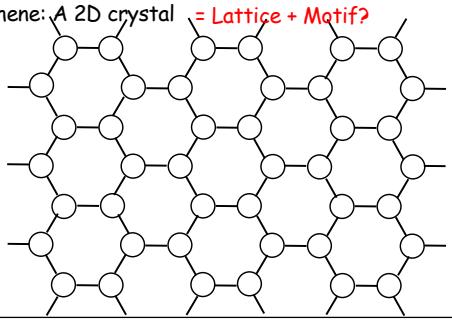
Graphene: A 2D crystal = Lattice + Motif?



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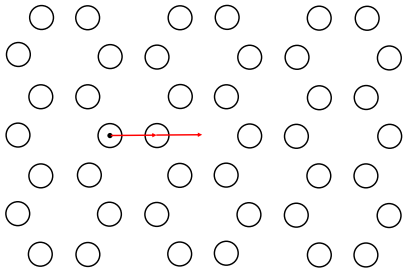
Graphene: Are the centres of all atoms lattice points?



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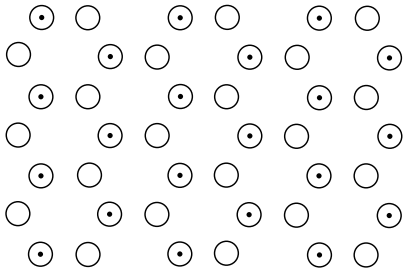
Graphene: Only the centres of alternate atoms are lattice points



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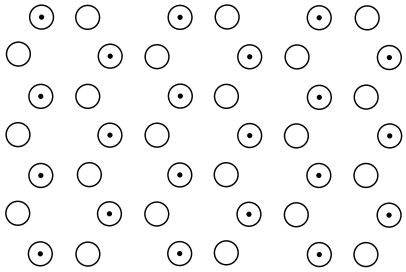
Lattice of graphene



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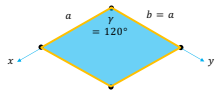
Unit cell of the lattice of Graphene

primitive hexagonal lattice

hp



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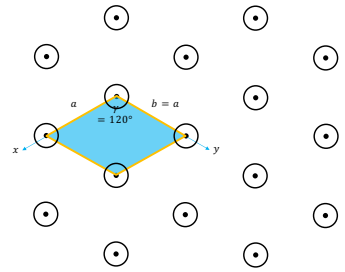
How to build crystal of graphene from its lattice?

Single atom per lattice point of an hp lattice is not graphene.

primitive hexagonal lattice
hp



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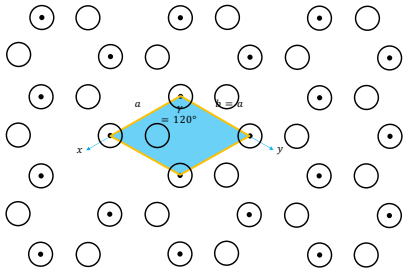
How to build crystal of graphene from its lattice?

Primitive hexagonal Lattice: *hp*

For 2D lattice we use small p
hp: 2D Primitive Hexagonal

For 3D lattice we use Capital P
hP: 3D Primitive Hexagonal



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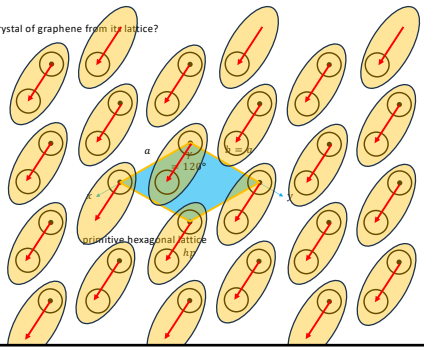
How to build crystal of graphene from its lattice?



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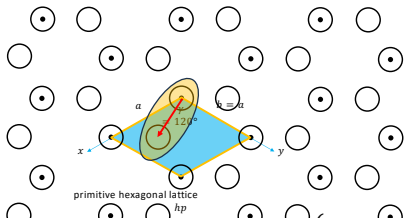
How to build crystal of graphene from its lattice?



$$Graphene = hp\ lattice + 2\ atom\ motif \begin{cases} C\ 0\ 0 \\ C\ \frac{2}{3}\ \frac{1}{3} \end{cases}$$

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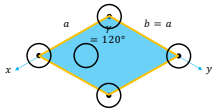
Unit cell of graphene: primitive or nonprimitive?

Two atoms per cell = $\frac{1}{4}\times 4 + 1$



One lattice point per cell = $\frac{1}{4}\times 4 \Rightarrow Primitive$

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Pitfall
Primitive vs. Nonprimitive unit cell

Primitive unit cell contains ONE LATTICE POINT **per cell**

And NOT one atom per cell.

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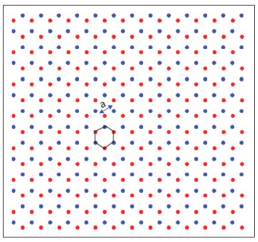
Figure 1. The lattice structure of graphene has hexagonal symmetry as indicated by the red and blue colored 'atoms' taken together. This class of lattice is not a Bravais lattice but can be constructed from two interpenetrating lattices of equilateral triangles.



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Every lattice has to be a Bravais lattice.

Bravais lattice is a classification of lattices.

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Description of Motif

An atom or a group of atoms associated with each lattice point

1. No. of atoms
2. Chemical identity of atoms
3. Location of atoms

   Displacement coordinates with respect to the lattice point in the crystal coordinate system (fractional coordinates)

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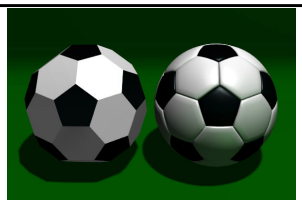

Truncated Icosahedron

Icosahedron: A Platonic solid (a regular solid)

Truncated Icosahedron: An Archimedean solid

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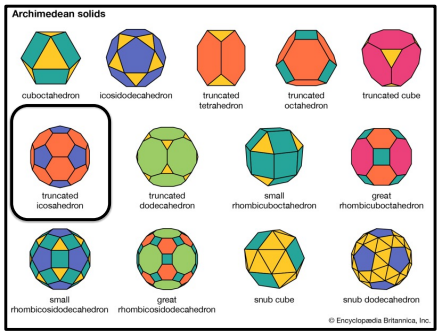

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Other closed-shell fullerenes

C70
C76
C78
C84

All closed-shell fullerenes have 12 pentagonal faces.

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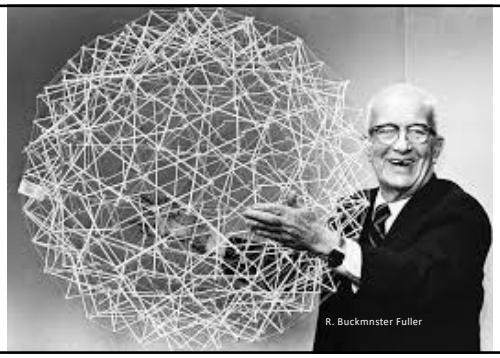

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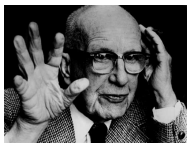

American architect, author, designer, futurist, inventor, and visionary.

He was expelled from Harvard twice:

1. first for spending all his money partying with a Vaudeville troupe,
2. for his "irresponsibility and lack of interest".

what he, as an individual, could do to improve humanity's condition, which large organizations, governments, and private enterprises inherently could not do.

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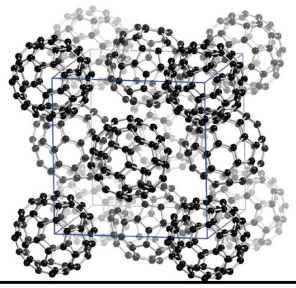
C60 Crystal = FCC lattice + C60 motif



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Carbon Nanotube

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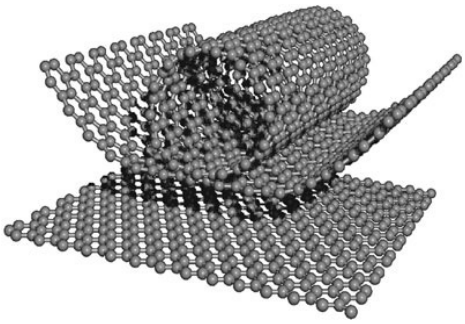

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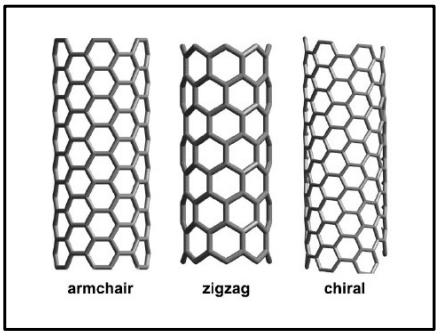

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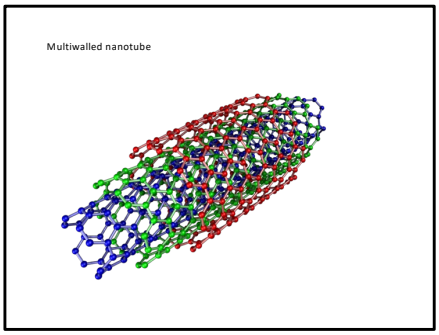

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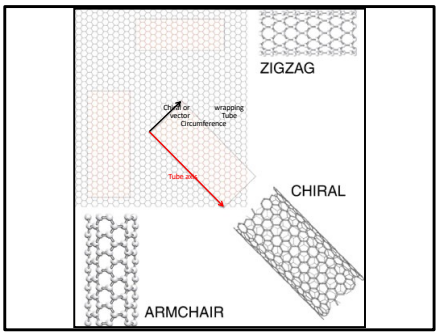

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Lecture 9
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Lecture 9

Nanotube
- Wrapping vector

Graphite: Lattice and Motif
Diamond: lattice and Motif
Close-Packing of spheres: 1D

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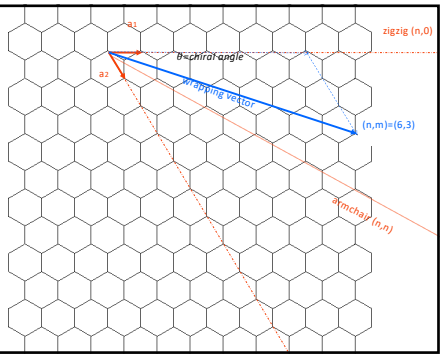
Wrapping vector description of nanotube:
(n, m)



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Electrical
For a given (*n*,*m*) nanotube, if *n* = *m*, the nanotube is metallic;

if *n* − *m* is a multiple of 3, then the nanotube is semiconducting with a very small band gap,

otherwise the nanotube is a moderate semiconductor.

Thus all armchair (*n*=*m*) nanotubes are metallic,

and nanotubes (5,0), (6,4), (9,1), etc. are semiconducting.

In theory, metallic nanotubes can carry an electrical current density of 4×10^9 A/cm2 which is more than 1,000 times greater than metals such as copper[23].

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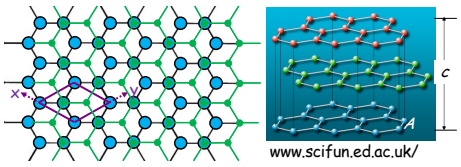
Graphite

a = 2.46 Å
c = 6.70 Å



www.scifun.ed.ac.uk/

Lattice: Simple Hexagonal

Motif: 4 carbon atoms

000; 2/3 1/3 0; 2/3 1/3 1/2; 1/3 2/3 1/2

Proof:Left as an exercise

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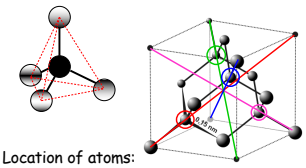
Diamond

Sp^3 hybridization ⇒ 4 covalent bonds
⇒ Tetrahedral bonding



Location of atoms:

8 Corners

6 face centres

4 one on each of the 4 body diagonals

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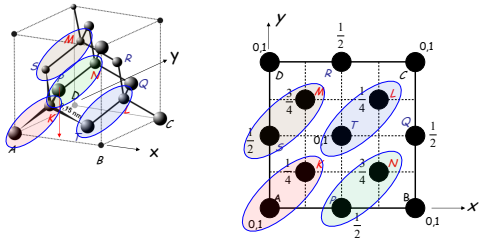
Diamond Cubic Crystal: Lattice & motif?



Diamond Cubic Crystal
= FCC lattice + motif: 000; $\frac{1}{4}\frac{1}{4}\frac{1}{4}$

Projection of the unit cell on the bottom face of the cube

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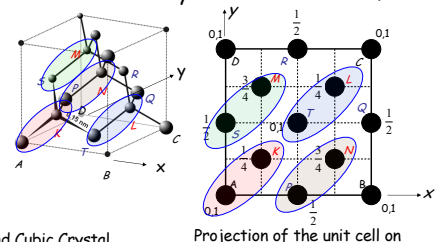
Diamond Cubic Crystal: Lattice & motif?



Diamond Cubic Crystal
= FCC lattice + motif: 000; $\frac{1}{4}\frac{1}{4}\frac{1}{4}$

Projection of the unit cell on the bottom face of the cube

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Pitfall 1D: Diamond Cubic Lattice

~~Diamond Cubic Lattice~~

Diamond Cubic Crystal Structure = FCC Lattice + 2 atom Motif $\begin{cases} 000 \\ \frac{1}{4}\frac{1}{4}\frac{1}{4} \end{cases}$

There are only three Bravais Lattices: SC, BCC, FCC.

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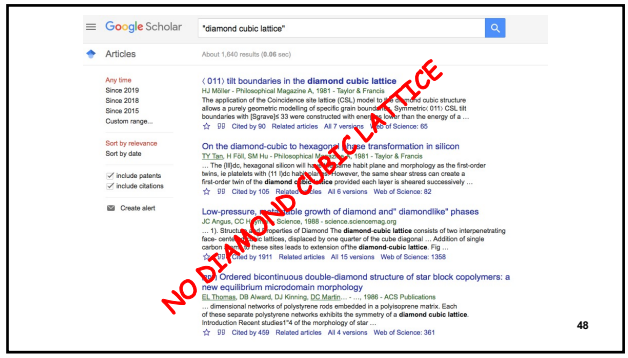

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~~Diamond Cubic Lattice~~

Diamond Cubic Crystal

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Metals and Alloys

1. Metallic bond: Nondirectional (Fact)

   ⇒As many bonds as geometrically possible (to lower the energy)

   ⇒ Close packing

2. Atoms as hard sphere (Assumption)

3. Elements (identical atoms)

1, 2 & 3 ⇒ Elemental metal crystals: close packing of equal hard spheres

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Close packing of equal hard spheres

Arrangement of equal nonoverlapping spheres to fill space as densely as possible

Sphere packing problem:
What is the densest packing of spheres in 3D?

Kepler's conjecture, 1611 $P.E = \frac{\pi}{3\sqrt{2}} = 0.74$

Kissing Number Problem

What is the maximum number of spheres that can touch a given sphere?

Coding Theory

Internet data transmission

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Close packing of equal hard spheres

1-D packing

A chain of spheres

P.E.= $\frac{occupied\ length}{total\ length}$ =1 Kissing Number= 2

Close-packed direction of atoms

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Lecture 10
Th 13.08.2025
(as Friday)

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Close packing of equal hard spheres

1-D packing

A chain of spheres

P.E.= $\frac{occupied\ length}{total\ length}$ =1 Kissing Number= 2

Close-packed direction of atoms

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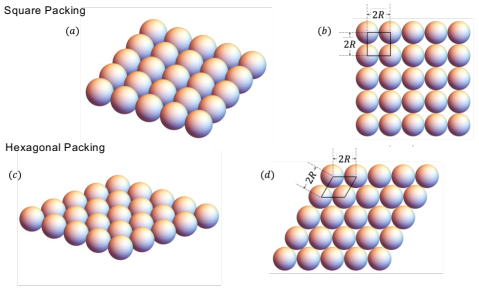

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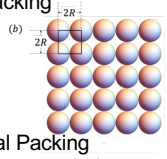
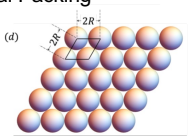
$$2\,D\ Packing\ Efficiency\ (PE) = \frac{Area\ occupied}{Total\ Area}$$

Square Packing



$$PE = \frac{\pi}{4} \approx 0.78$$

Hexagonal Packing



$$PE = \frac{\pi}{4} \approx 0.78$$

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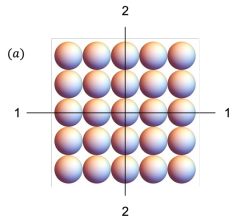

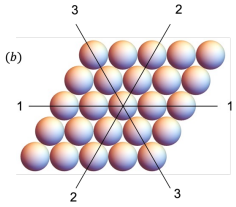

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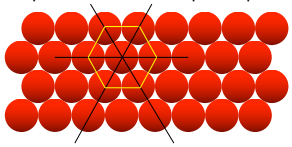
Close packing of equal hard spheres

2-D packing

A hexagonal layer of atoms Close-packed plane of atoms



Close-packed directions? **3**

P.E.= $\frac{occupied\ area}{total\ area} = \frac{\pi}{2\sqrt{3}} = .907$ Kissing Number=6

1940 L. Fejes Toth : Densest packing of circles in plane

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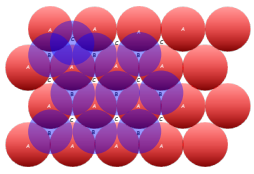
Close packing of equal hard spheres

3-D packing



First layer A

Second layer B

Third layer A or C

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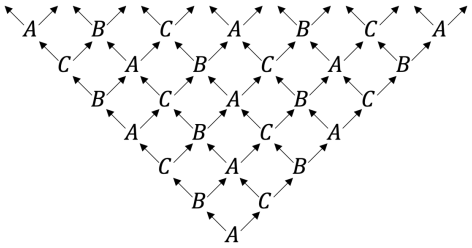
All Possible stacking sequences giving rise to closest packing



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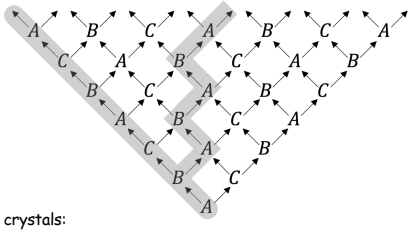
Two important close packing realized in nature

ccp hcp



Close packed crystals:

...ABABAB... Hexagonal close packed (HCP)
...ABCABC... Cubic close packed (CCP)

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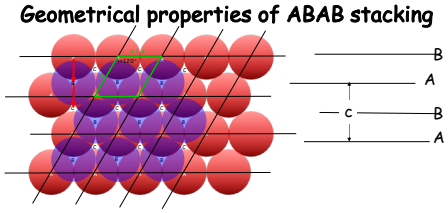
Geometrical properties of ABAB stacking



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≠c; α=β=90°, γ=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

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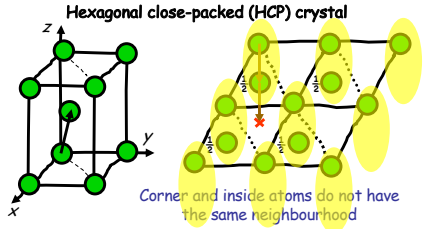
Hexagonal close-packed (HCP) crystal



Corner and inside atoms do not have the same neighbourhood

Lattice: Simple hexagonal

Motif: Two atoms: 000; 2/3 1/3 1/2

hcp lattice ✗

hcp crystal ✓

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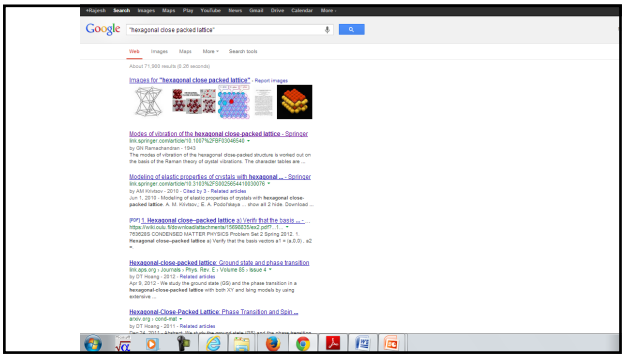

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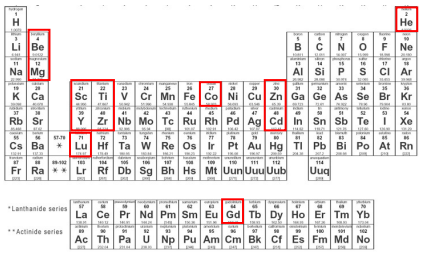
Hexagonal Close-Packed Crystal Structures



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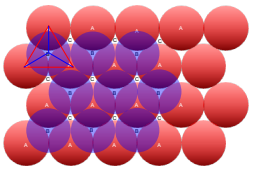
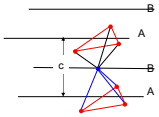
c/a ratio of an ideal HCP crystal





A single B atom sitting on a base of three A atoms forms a regular tetrahedron with edge length $a = 2R$

The same B atom also forms an inverted tetrahedron with three A atoms sitting above it

c = 2 × height of a tetrahedron of edge length a

$$\frac{c}{a} = \frac{2\sqrt{2}}{\sqrt{3}} \cong 1.633..$$

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Some HCP crystals

Element	c/a
Be	1.567
Ti	1.587
Mg	1.623
Idea HCP	1.633
Zn	1.856
Cd	1.886

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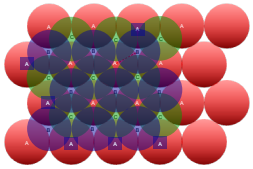
Geometrical properties of ABCABC stacking



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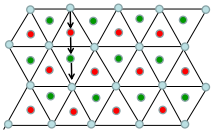
Geometrical properties of ABCABC stacking

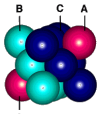


All atoms are equivalent and their centres form a lattice

Motif: single atom 000

What is the Bravais lattice?

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



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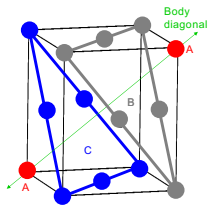
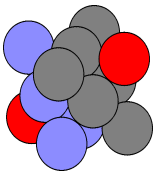
Close packed planes in the FCC unit cell of cubic close packed crystal





Close packed planes: {1 1 1}

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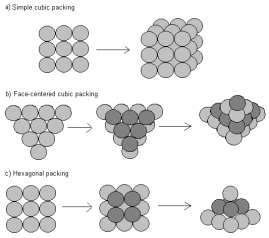
Find the mistake in the following figure from a website:



http://www.tiem.utk.edu/~gross/bioed/webmodules/spherefig1.gif

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Table 5.1

Coordination Number and Packing Efficiency

	CW	HW
Crystal Structure	**Coordination number**	**Packing efficiency**
Diamond cubic (DC)	4	0.32
Simple cubic (SC)	6	0.52
Body-centred cubic	8	0.68
Face-centred cubic	12	0.74

Empty spaces are distributed in various **voids**

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