MLL 100

Introduction to Materials Science and Engineering

TWF 10:00-11:00

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IIT Delhi
Department of Materials Science and Engineering

January 04, 2022

Lecture 1: Introduction

Course Policy

- Evaluation scheme (Grading)
- Attendance Policy
- Suggested Readings
- Introductory lecture

COURSE POLICY

Evaluation scheme

3 + 1 = 4 credits

3-0-2

Laboratory session (Demonstration/Take-home assignment Total experiments: 8)	25%
Quiz (Moodle Total: 4)	25%
Minor Exam (Moodle)	25%
Major Exam (Moodle)	25%

Laboratory session (Demonstration/Take-home assignment Total experiments: 8)	**25%**

- Total lab experiments: 8
- **Each take-home lab experiment will be uploaded on Moodle on Friday at 5:00 p.m. and will be due by 5:00 p.m. on Friday the week after.**
- NO LATE SUBMISSIONS WILL BE ENTERTAINED. Zero marks will be given for late submissions.
- All the take home assignments and lab sheets should be submitted in Moodle. Clear instructions will be given. If you violate instructions, marks will be deducted accordingly.
- Any query related to grading of lab experiments and take home assignments should be asked to the corresponding TAs.
- Any kind of cheating or unfair means during the exams (Quiz, minor, major) may lead to strong disciplinary action which may result **FAILING** in the entire course.

Quiz (Moodle Total: 4)	**25%**

- On Moodle, with minimum 1 day notice.
- Each quiz will be of *20 minutes* duration, held during regular class slots and multiple choice questions/one word answers only. No long answer type questions will be asked.
- Negative marking will be implemented: *-0.25 for every incorrect answer*.
- Once you see a question, you will *NOT be allowed to go back and attempt* the question again, or correct your answers.
- **No make up quizzes will be given. All quizzes will contribute to your 25% score.**

Minor Exam (Moodle)	**25%**
Major Exam (Moodle)	**25%**

- Minor and Major examinations will be *conducted* on the specified dates *as per the institute calendar*.
- Both these exams will also be conducted *via Moodle*. The questions will be of mostly of *Numerical Type*. However, it will be notified, if there is any change in plan.
- *No negative marking will be implemented. There will be no answer options given either*.
- You will be allowed to go back and attempt the question again, or correct your answers.
- **No make up for Minor or Major exams will be taken. Such requests will not be considered.**

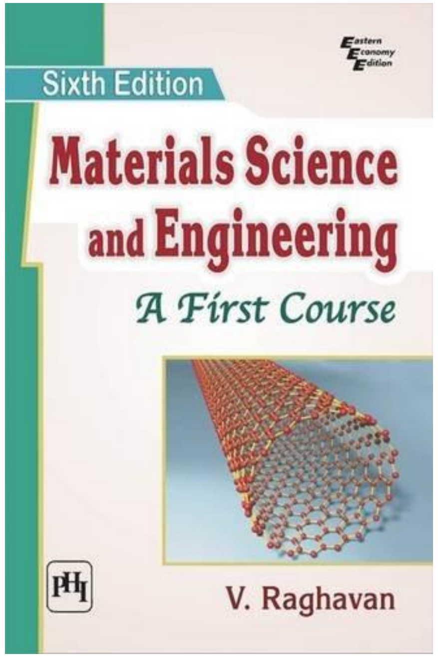
Attendance Policy

☺ No attendance policy

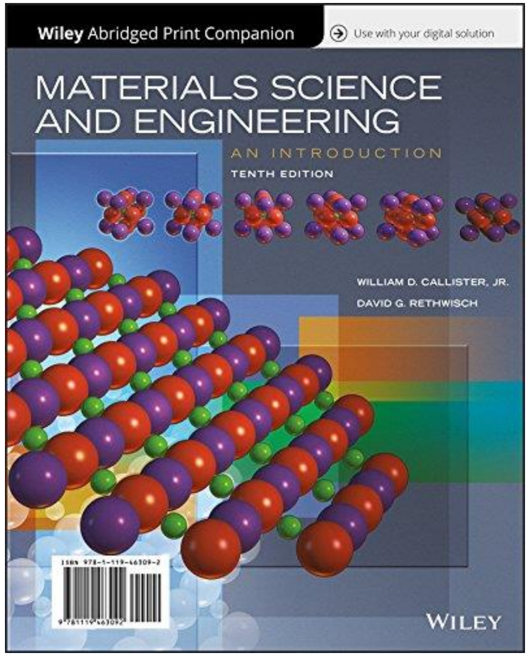
BUT ……………

Recommended studying from the suggested textbooks!

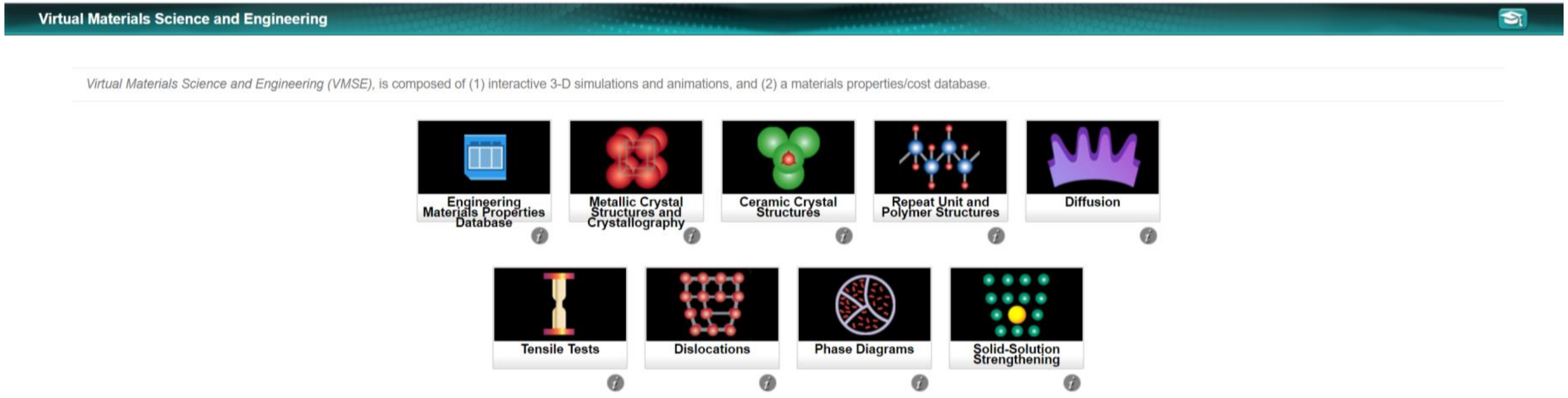
Reference Textbooks



- ❑ Materials Science and Engineering: A First Course; V. Raghavan
- ❑ Materials Science and Engineering: An Introduction by W.D. Callister, Jr., 7th edition, John Wiley and Sons.



- Virtual Material Science supplement https://wileyassets.s3.amazonaws.com/VMSE/index.html
- Lecture slides (pdf): Moodle



Why should I *enrol* myself for the course ‘Materials Science and Engineering’?

Why should I *learn* Materials Science and Engineering?

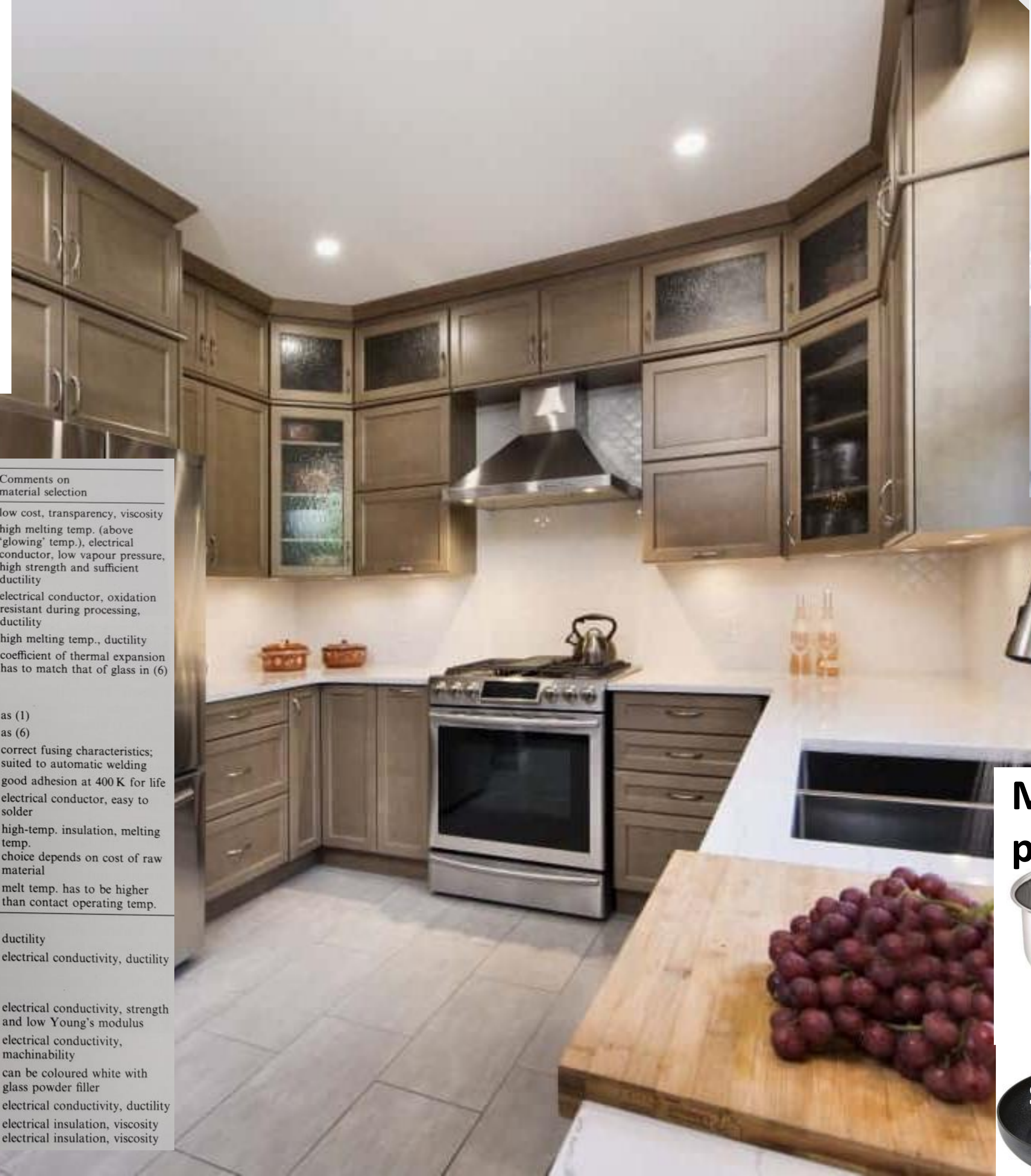
Three generations of light bulbs, each rated to produce 1100 lumens of light

Blow moulding of glass

Incandescent 75 Watts | Compact Fluorescent 18 Watts | LED 11 Watts

Tungsten filament wire of diameter ~ 15 μ

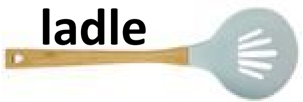
Part no.	Part name	Material	Main manufacturing processes	Comments on material selection
1	bulb	soda–lime glass	blow-moulding	low cost, transparency, viscosity
2	filament	tungsten	hot-pressing + wire-drawing	high melting temp. (above 'glowing' temp.), electrical conductor, low vapour pressure, high strength and sufficient ductility
3	lead-in wire	nickel or nickel-plated	wire-drawing (nickel plating)	electrical conductor, oxidation resistant during processing, ductility
4	filament support	molybdenum	wire-drawing	high melting temp., ductility
5	'dumet' wire	nickel-iron alloy	wire-drawing	coefficient of thermal expansion has to match that of glass in (6)
6	'pinch'	lead glass (SiO_2 + 20–30 wt% PbO)	pressing	
7	fuse sleeve	soda–lime glass	drawing	as (1)
8	exhaust tube	lead–glass	drawing	as (6)
9	fuse	copper–nickel alloy	wire-drawing + welding	correct fusing characteristics; suited to automatic welding
10	cement	phenol–formaldehyde		good adhesion at 400 K for life
11	outlead	copper or copper-clad steel	wire-drawing (electroplating)	electrical conductor, easy to solder
12	cap filling	opaque glass	casting	high-temp. insulation, melting temp.
13	cap	aluminium or brass	pressing	choice depends on cost of raw material
14	contacts	solder (Pb/Sn)		melt temp. has to be higher than contact operating temp.
holder				
15	insert	brass (70 Cu/30 Zn)	pressing	ductility
16	pins	brass (60 Cu/40 Zn)	extrusion	electrical conductivity, ductility
17	holder	phenol-formaldehyde (filled with wood/paper)	compression moulding	
18	spring	phosphor bronze (Cu/6Sn/0.2 P)	wire-drawing	electrical conductivity, strength and low Young's modulus
19	connector block	brass (60 Cu/40 Zn)	forging + machining	electrical conductivity, machinability
20	cover	urea-formaldehyde (filled with glass)		can be coloured white with glass powder filler
21	conductor	copper	wire-drawing	electrical conductivity, ductility
22	twin core	PVC (plasticized)	extrusion	electrical insulation, viscosity
23	flex	PVC (plasticized)	extrusion	electrical insulation, viscosity



Faucet

Metallic pan

Polymer ladle

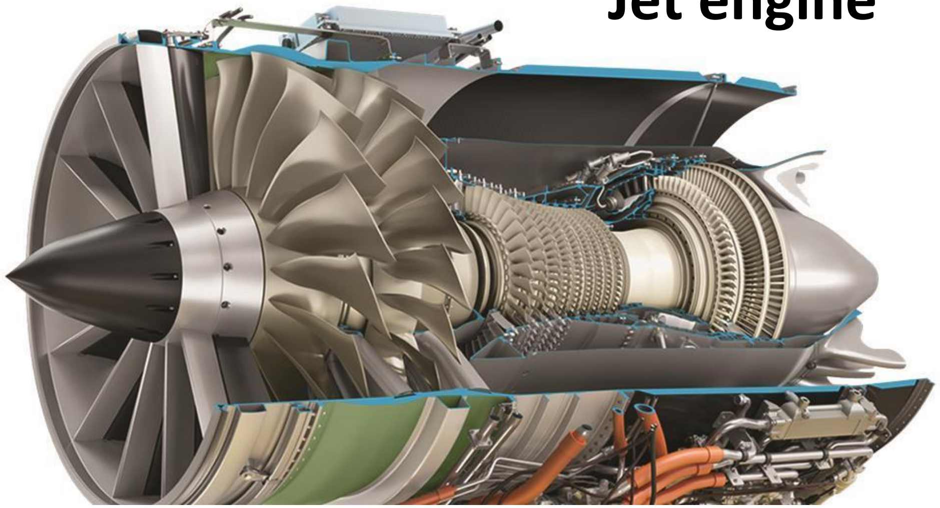


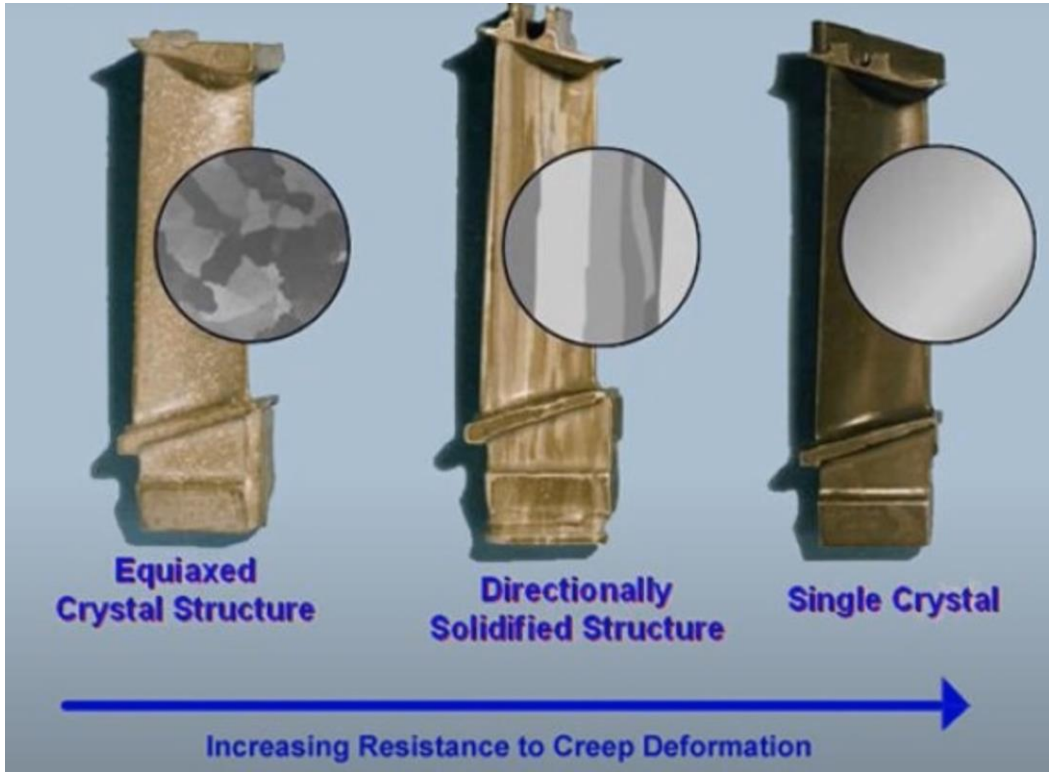
Non-stick pan

Wooden spoon

Bicycle frames

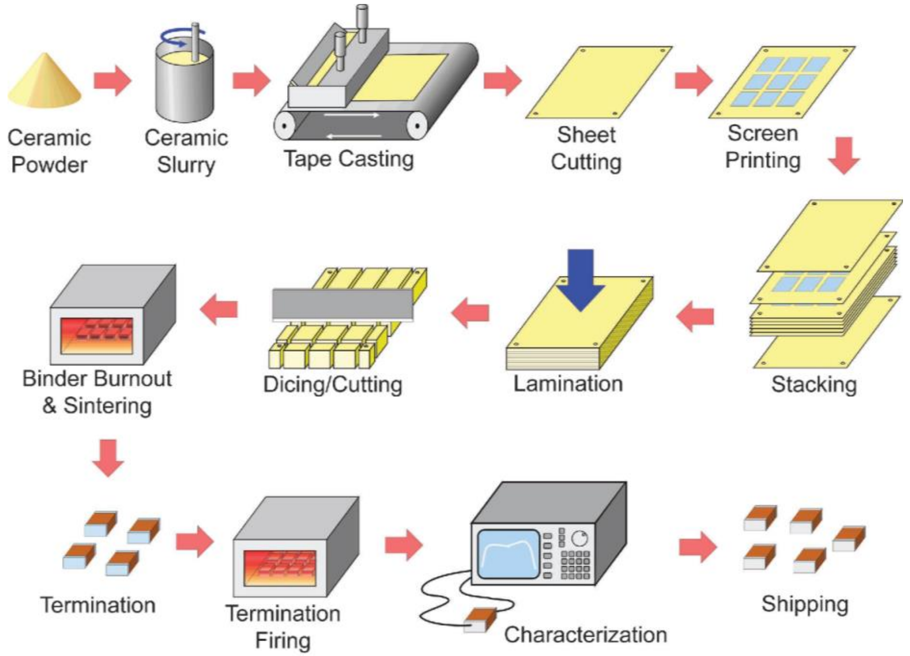
Jet engine





Fun watch

[Evolution of jet engine turbine blades]



Cleanroom

Semiconductor industry

Microscope

Which type of cup will you go for to enjoy your sip of tea?

Steel

Ceramic

Polymer

Cardboard

https://fast-poll.com/poll/1d2fa40c

https://fast-poll.com/poll/results/1d2fa40c

Which type of cup will you go for to enjoy your sip of tea?

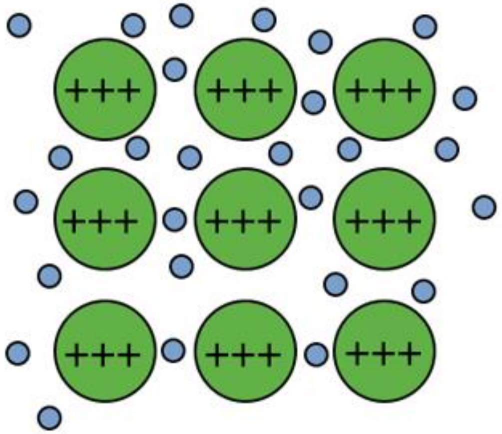
Steel

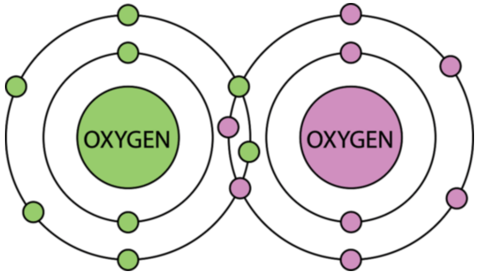
Ceramic

Polymer

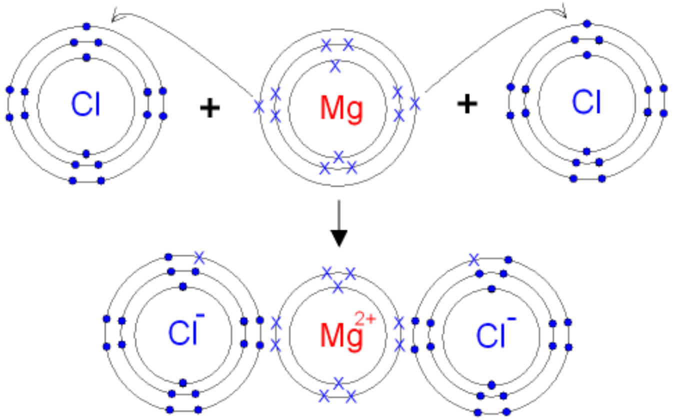
Cardboard

Metallic bonding



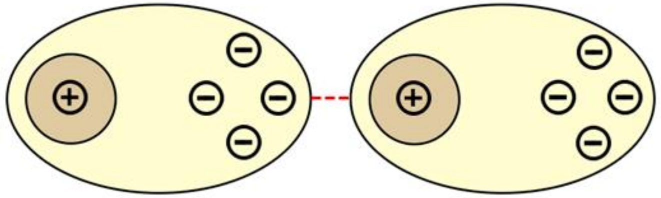


Covalent bonding

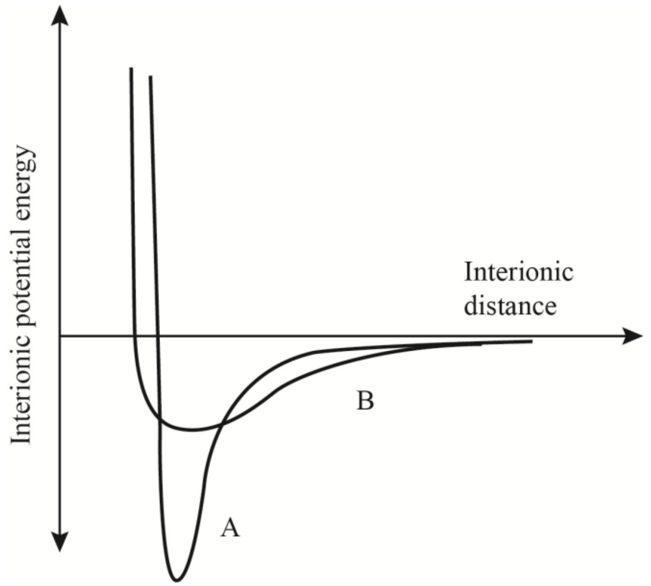


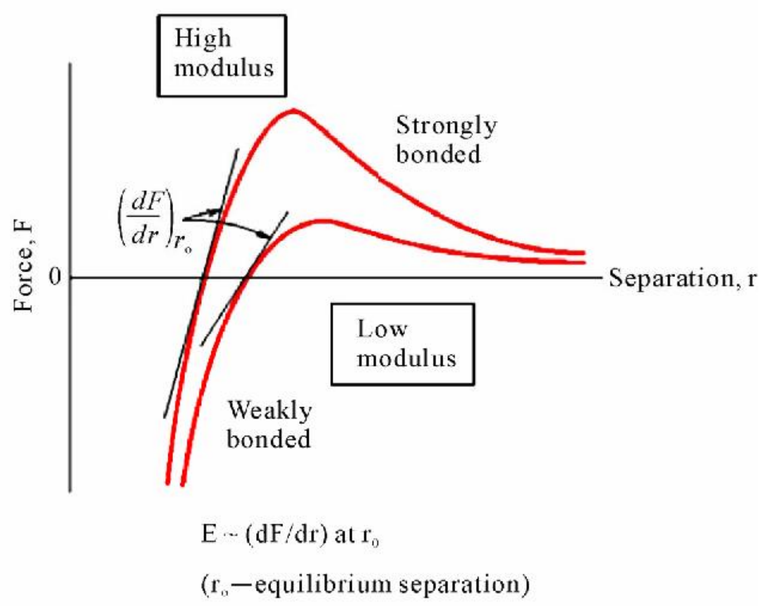
Ionic bonding

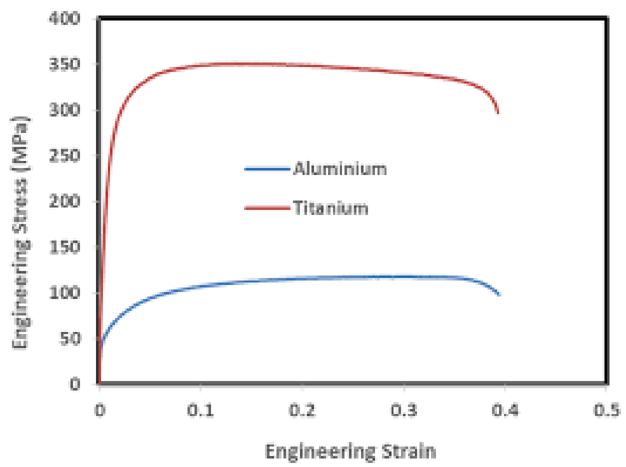
Van der waals' bonding



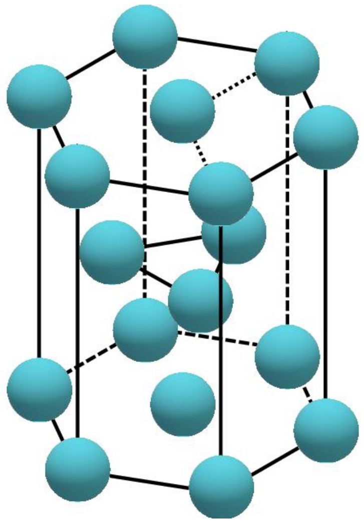
Does every material with metallic bonding exhibit similar properties?

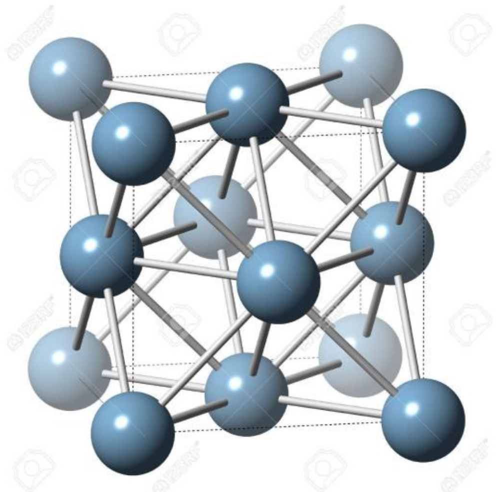






Structure

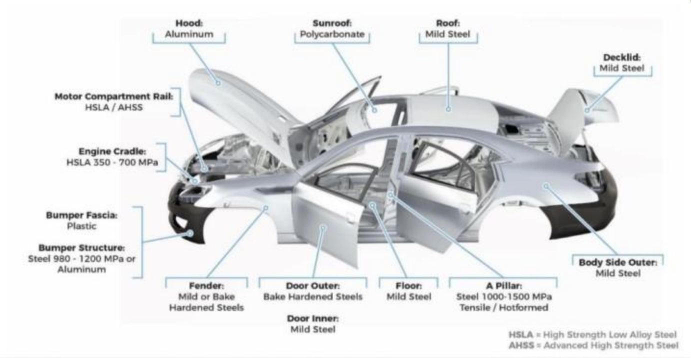




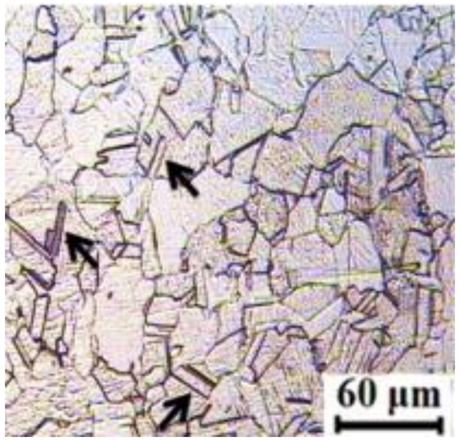
Structure of materials

☛ What do you mean by ‘Structure’?

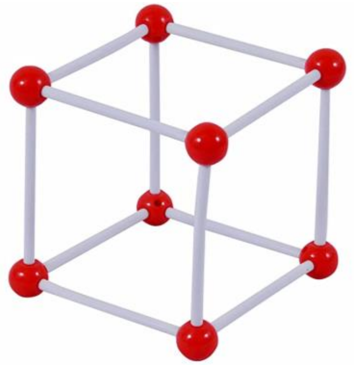
Quantitative description of arrangement of internal constituents in a material at different length scales



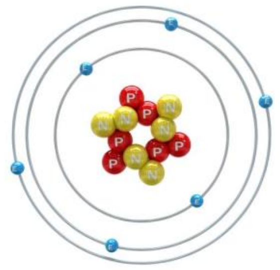
Macro-structure (> cm)



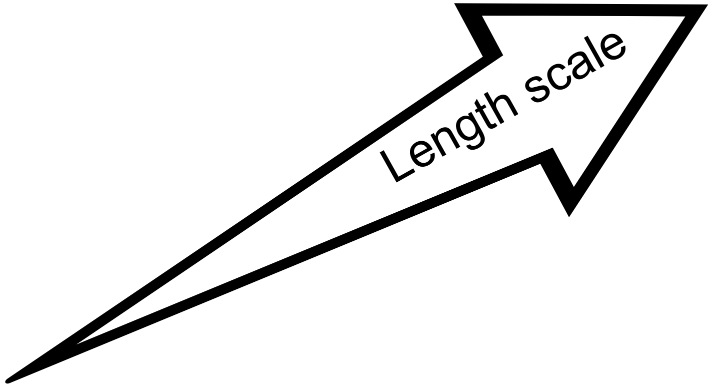
Micro-structure (μm)



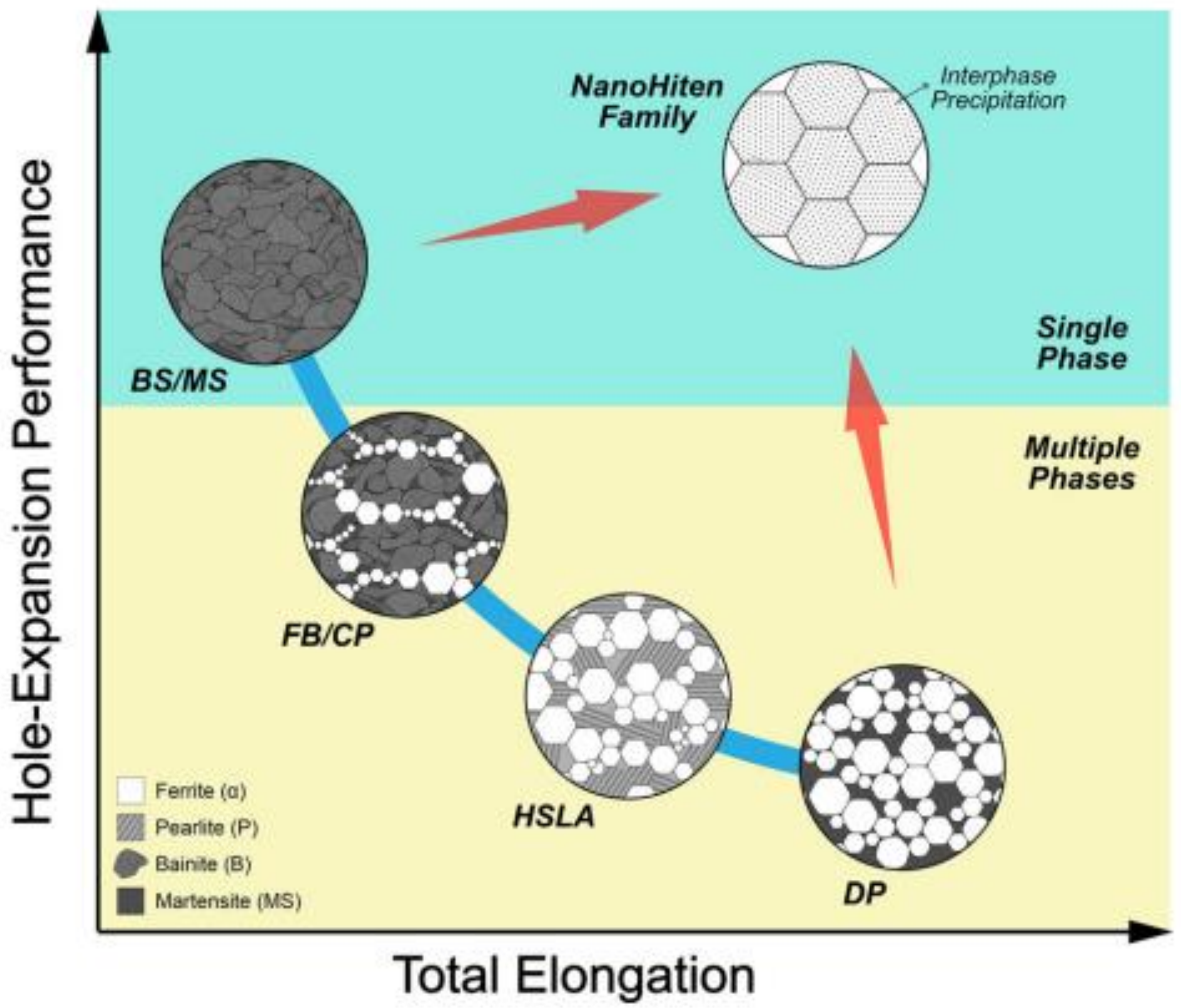
Crystal structure (Å)



Atomic structure (pm)



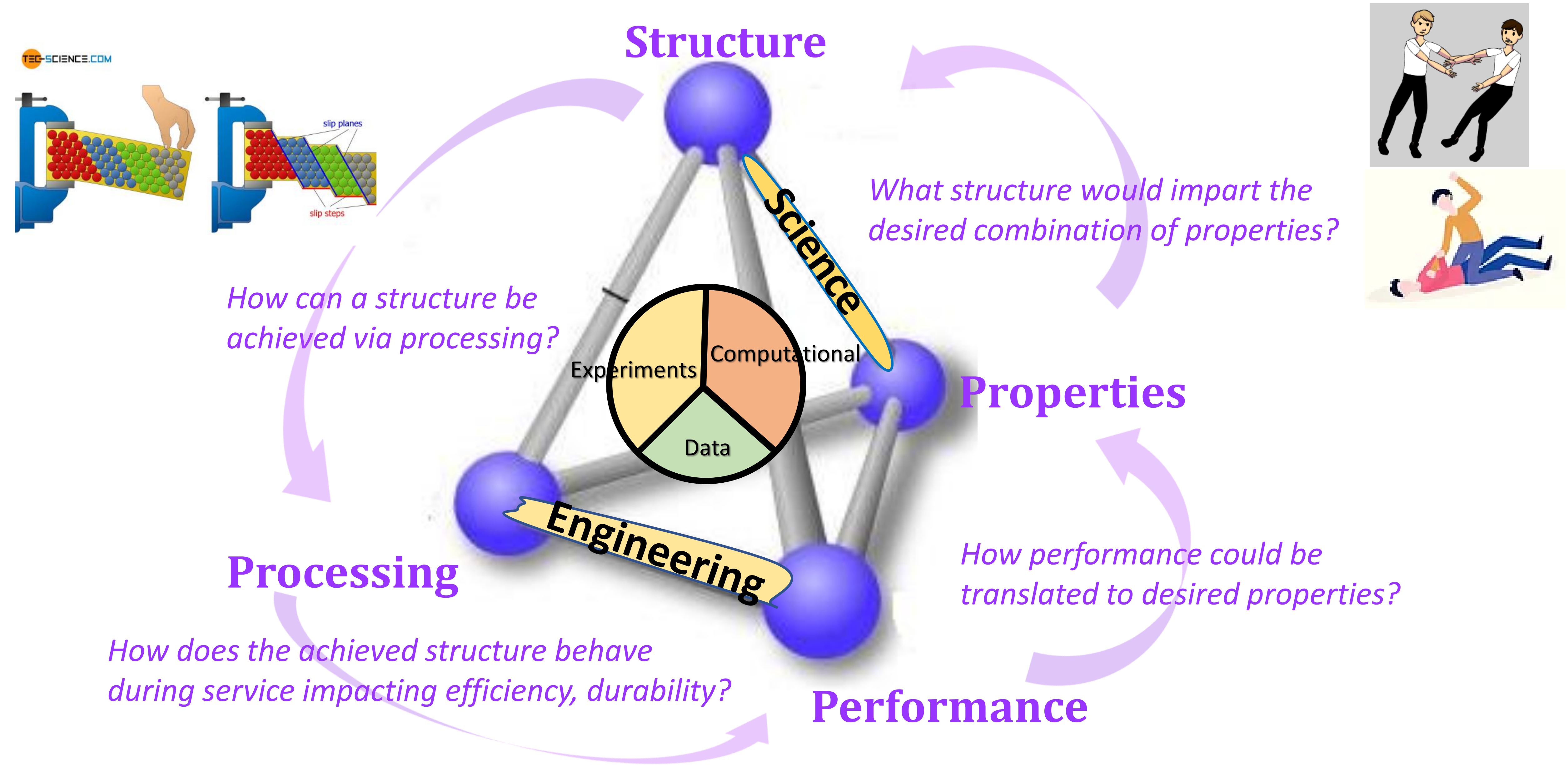
Can a single material exhibit different properties?



--------------- YES!

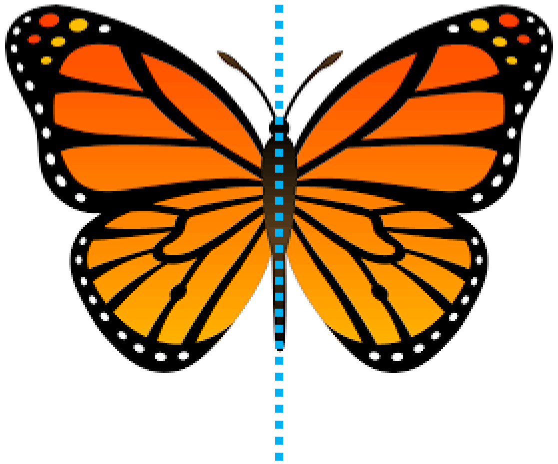
By carrying out different processing.

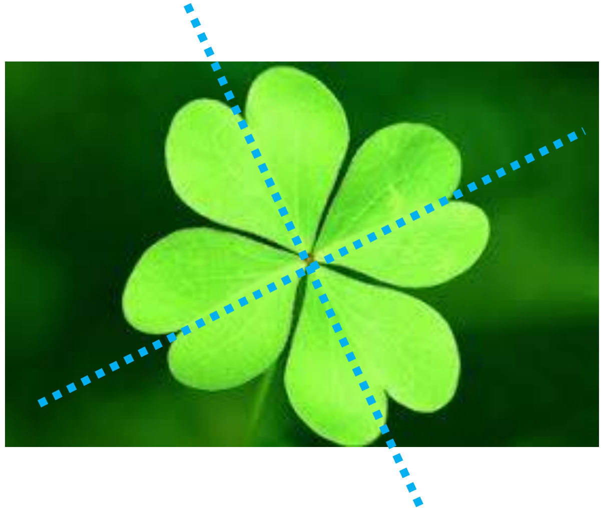
Structure of materials across different length scales to assess their **performance** and to control materials **properties** through **processing**.

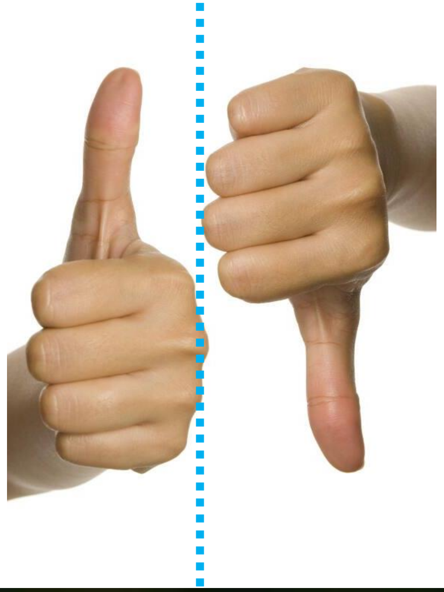


What are the factors which allow us to study crystal structure?

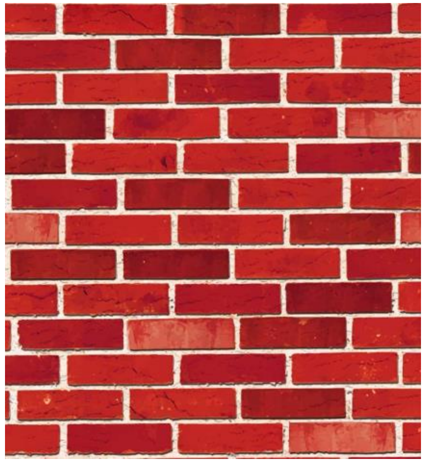
Symmetricity





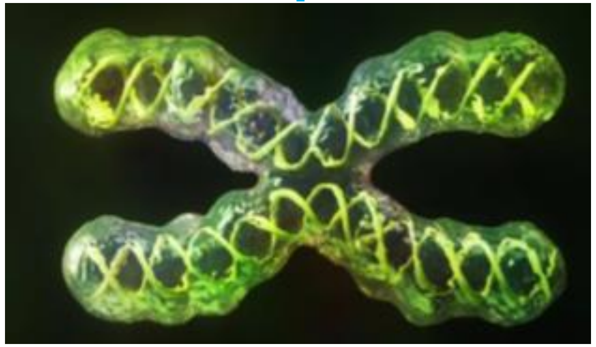


Periodicity



Brick patterns in wall

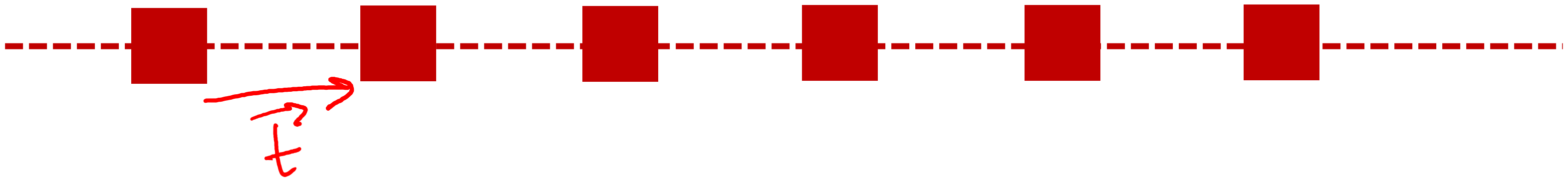
Honeycomb



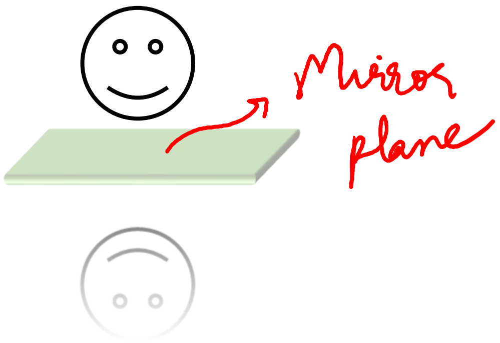
- Inversion
- Rotation
- Mirror
- Translation
- Glide

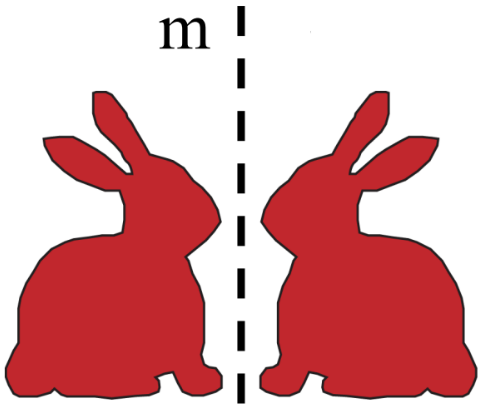
Symmetry

Translational



Reflectional





Rotational

$$n - fold = \frac{360^{\circ}}{n}$$

$1 - fold = \frac{360^{\circ}}{1}$

$2 - fold = \frac{360^{\circ}}{2}$

$3 - fold = \frac{360^{\circ}}{3}$

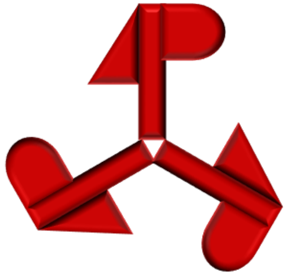
$4 - fold = \frac{360^{\circ}}{4}$

$6 - fold = \frac{360^{\circ}}{6}$

1-fold

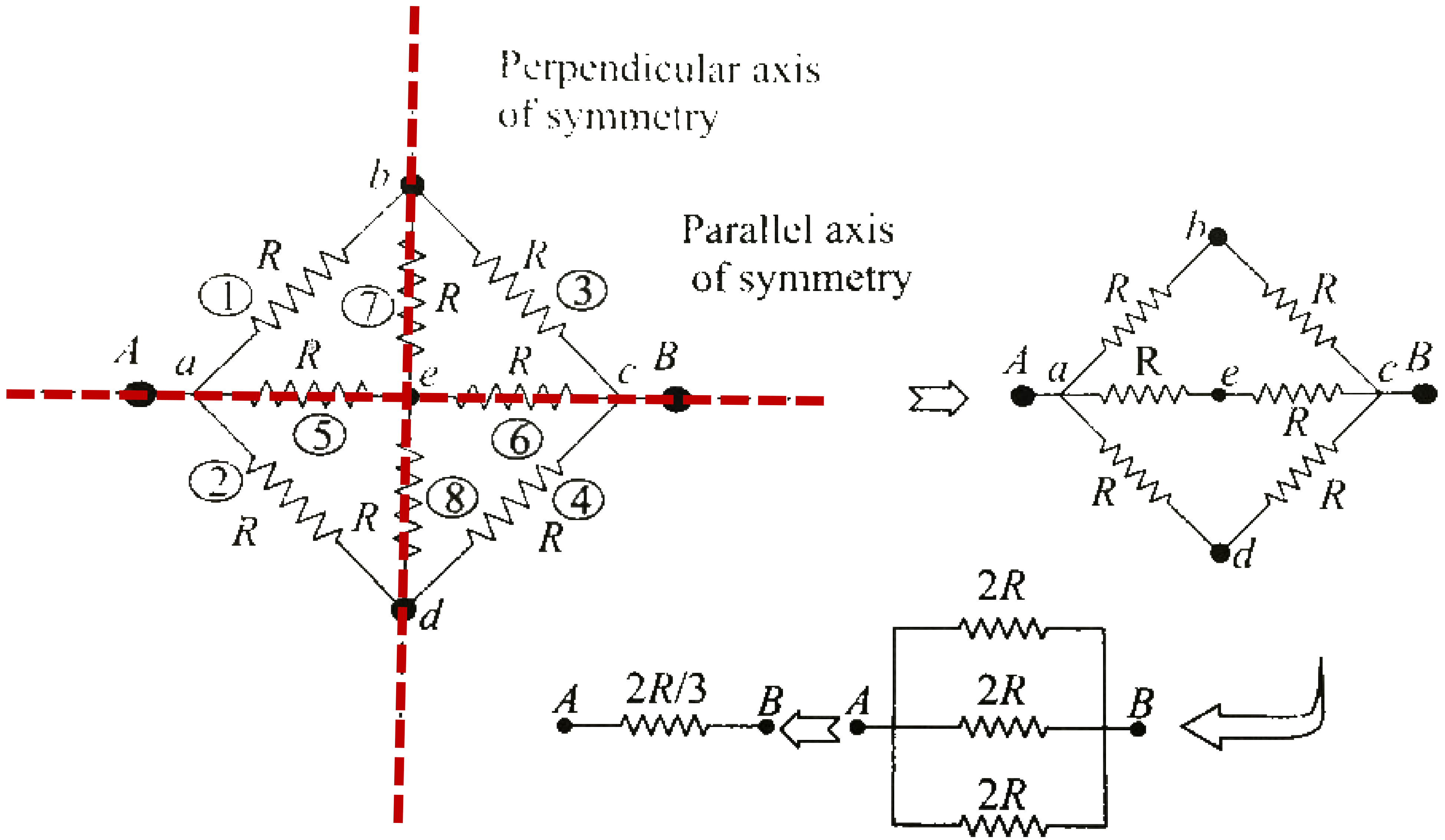
2-fold

3-fold



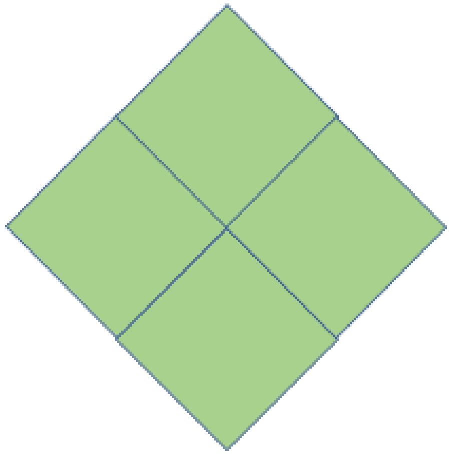
4-fold

6-fold

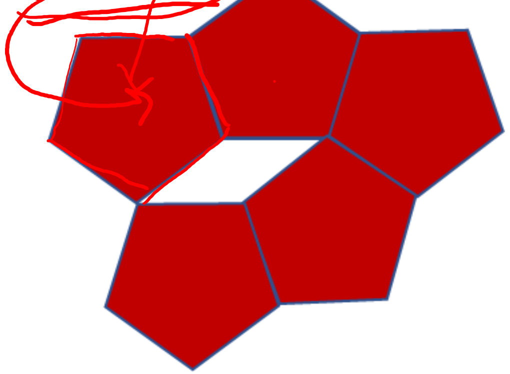

Perpendicular axis of symmetry
Parallel axis of symmetry
A
a
b
c
d
e
B
R
2R
2R/3

Why no mention of 5-fold rotational symmetry?

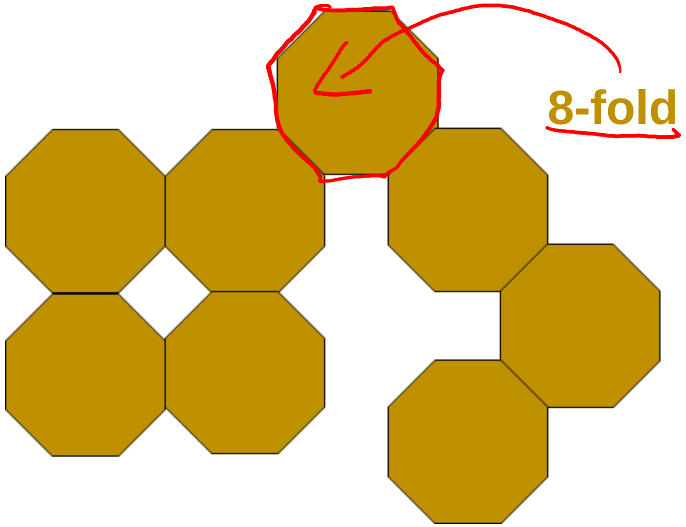
4-fold



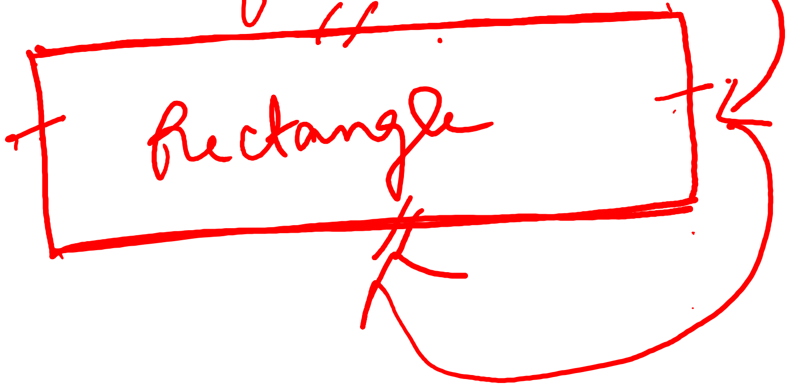
5-fold



8-fold



2-fold



Translational symmetry absent in long range

360°

4-fold

MLL 100

Introduction to Materials Science and Engineering

Lecture-2

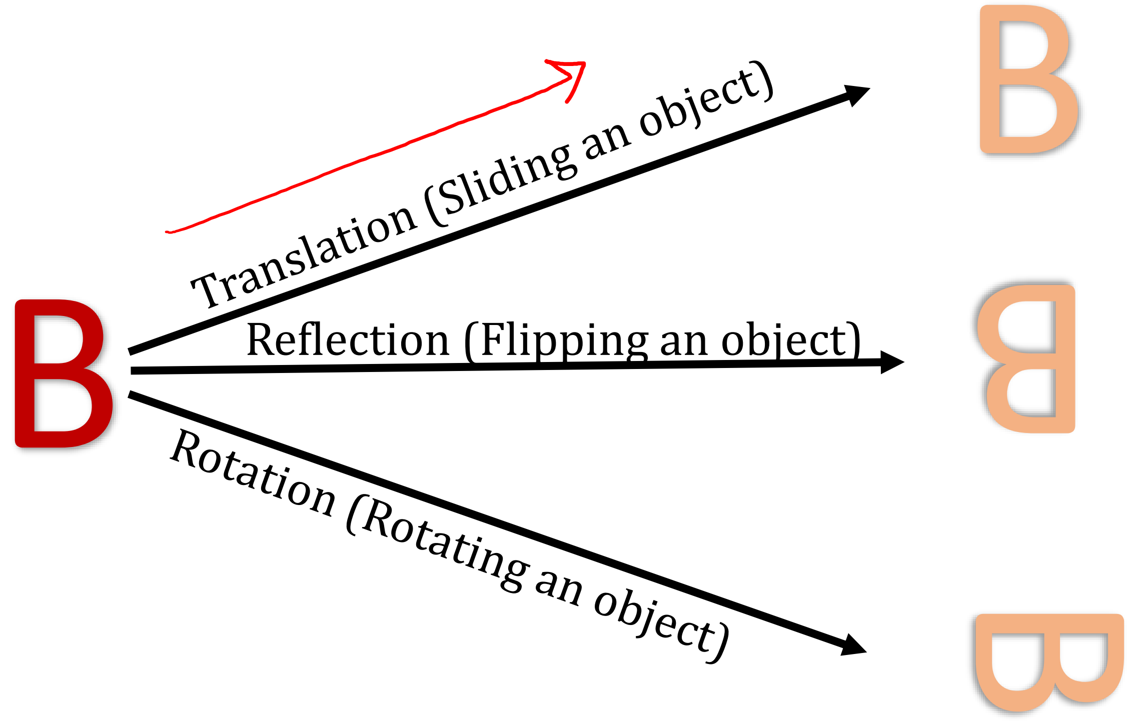
Dr. Sangeeta Santra (*ssantra@mse.iitd.ac.in*)

IIT Delhi
Department of Materials Science and Engineering

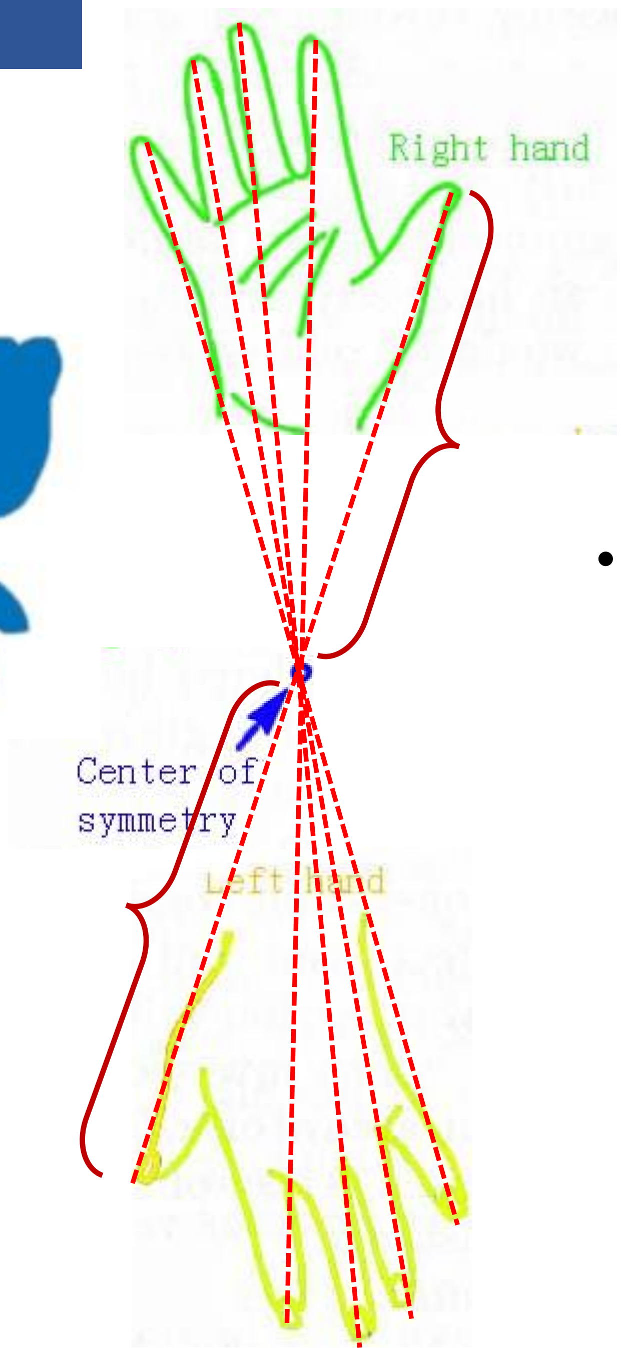
January 05, 2022

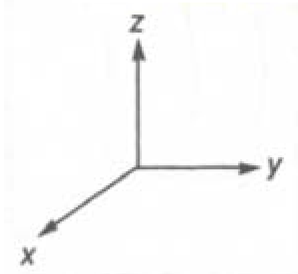
What we learnt in Lecture-1?

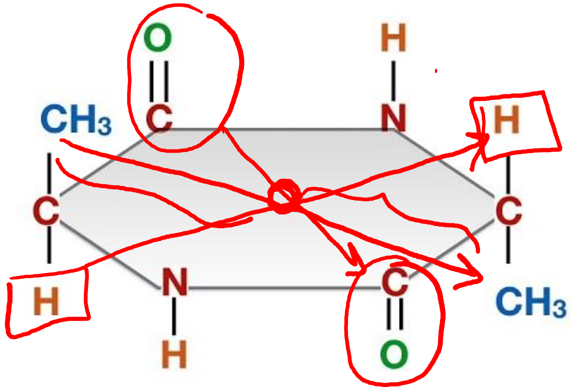
- Course Policy
- Structure of materials: Different length scales
- Symmetricity and periodicity



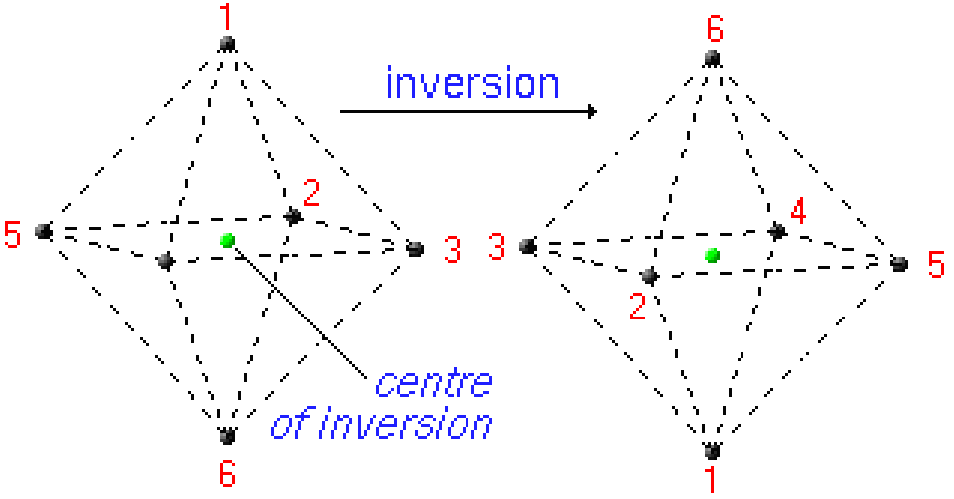
Inversion





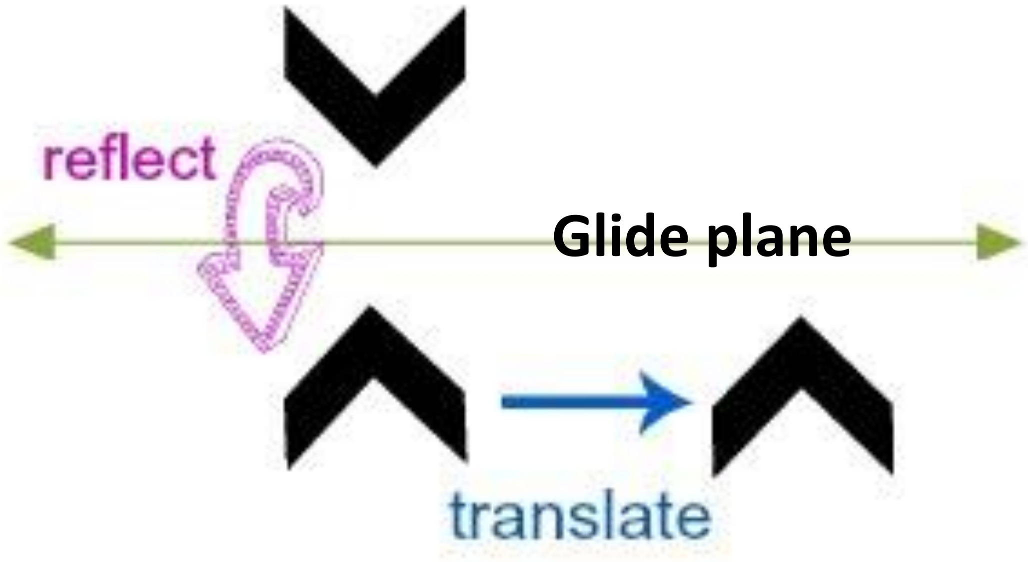


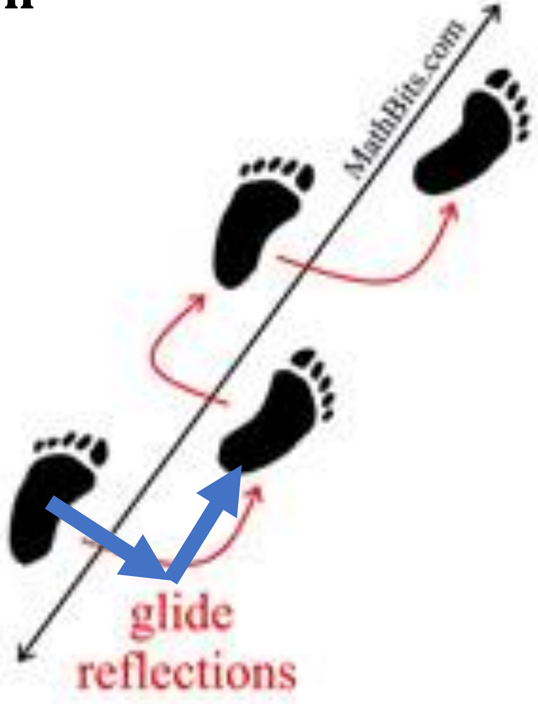
- An object at an equal and opposite distance through a single point ‘i’ after an inversion operation.

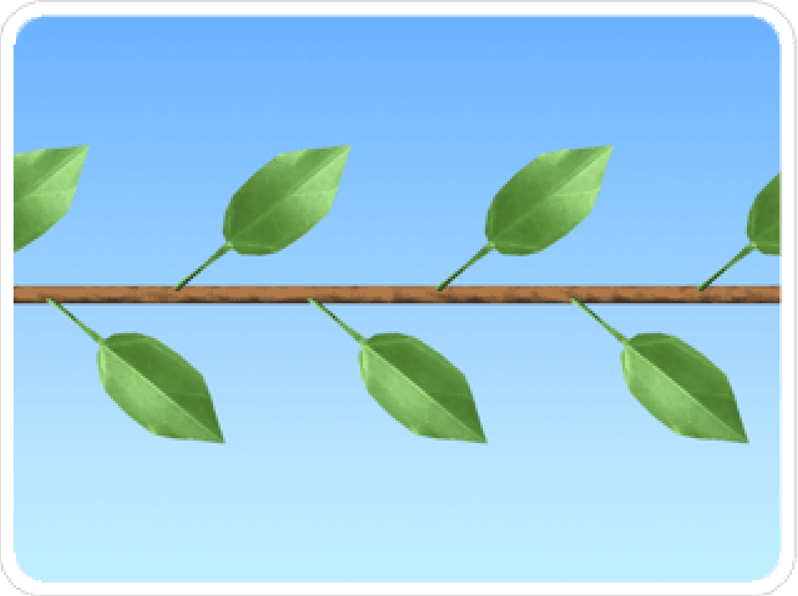


Glide

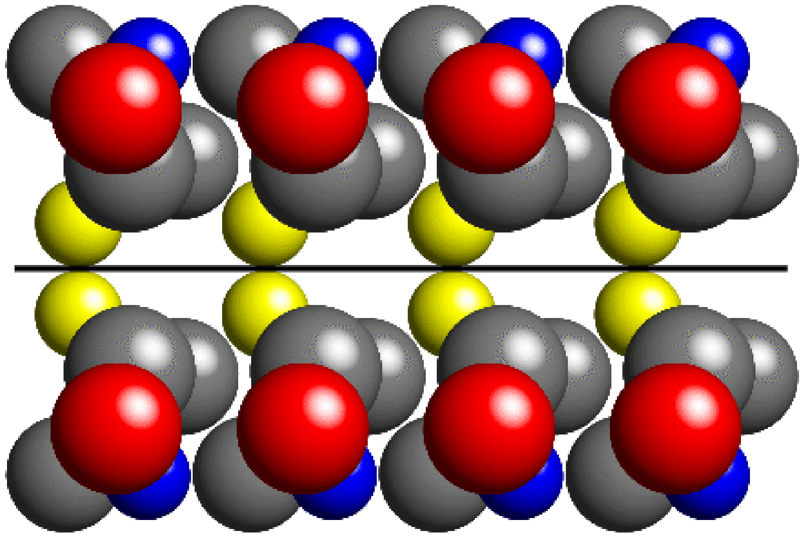
Glide = Reflection + Translation



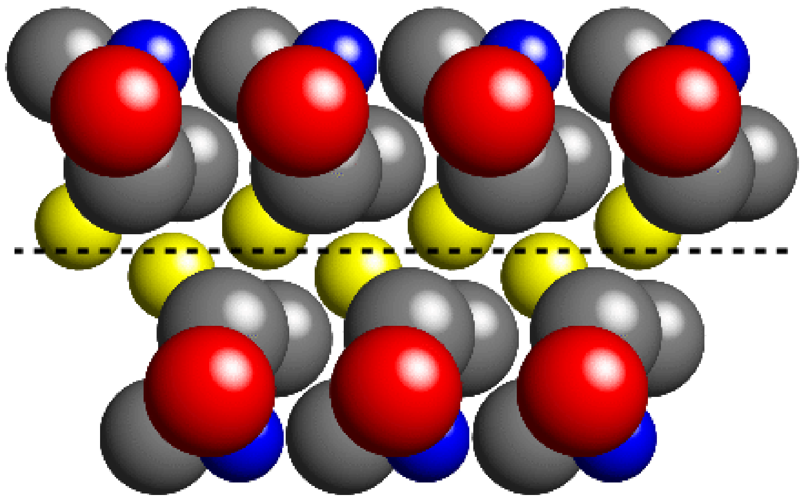




Mirror operation



Glide operation



Makes the molecular packing compact

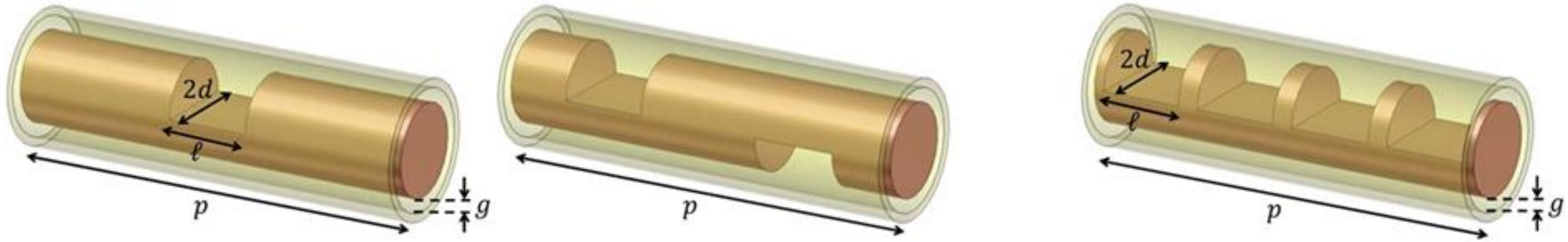
Glide Symmetries: an Additional Degree of Freedom to Control the Propagation Characteristics of Periodic Structures

Glide symmetry offers a compact, flexible solution for suppression of channel crosstalk in SSPP transmission lines

Twist and Polar Glide Symmetries: an Additional Degree of Freedom to Control the Propagation Characteristics of Periodic Structures

Fatemeh Ghasemifard, Martin Norgren & Oscar Quevedo-Teruel

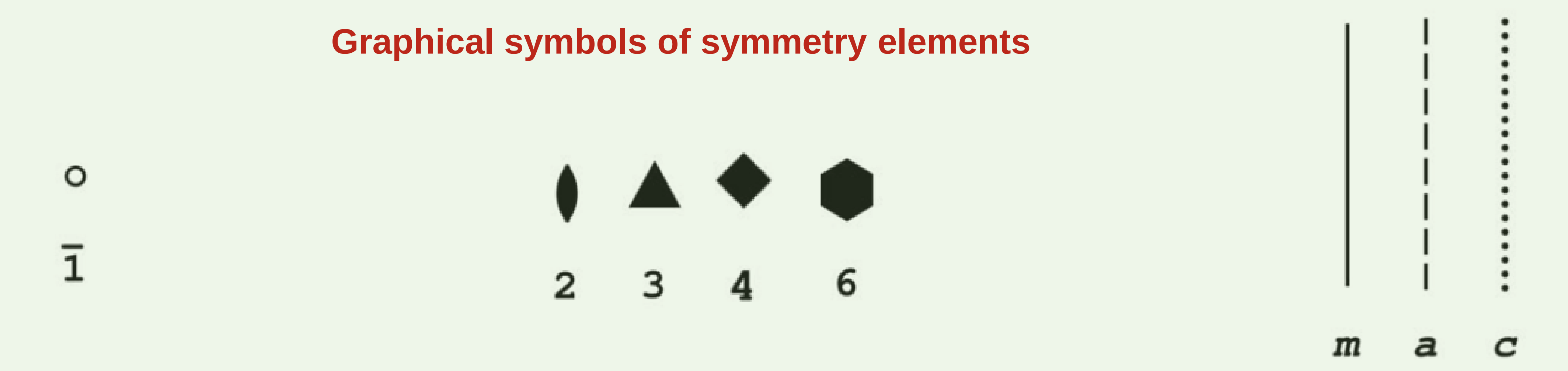
Scientific Reports **8**, Article number: 11266 (2018) | Cite this article



Graphical symbol of symmetry elements

*An object has **symmetry** if there is an operation, such as translation, rotation or reflection which maps the object onto itself, i.e., the object remains invariant after the transformation.*

- Symmetry:
  - Translational symmetry
  - Non-translational Symmetry (Inversion, Rotational and Reflectional)
  - Non-translational + Translational symmetry (Glide)



How many alphabets do you think has mirror symmetry?

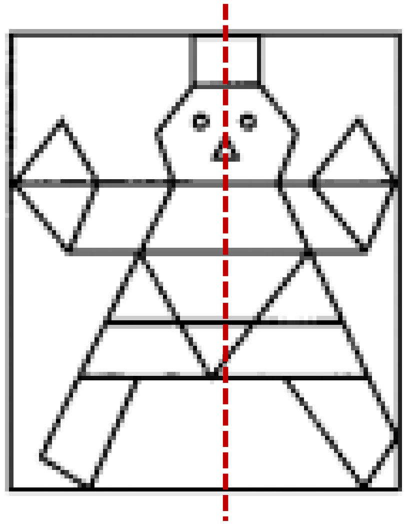
A, B, C, D, E, H, I, K, M,

O, T, U, V, W, X, Y

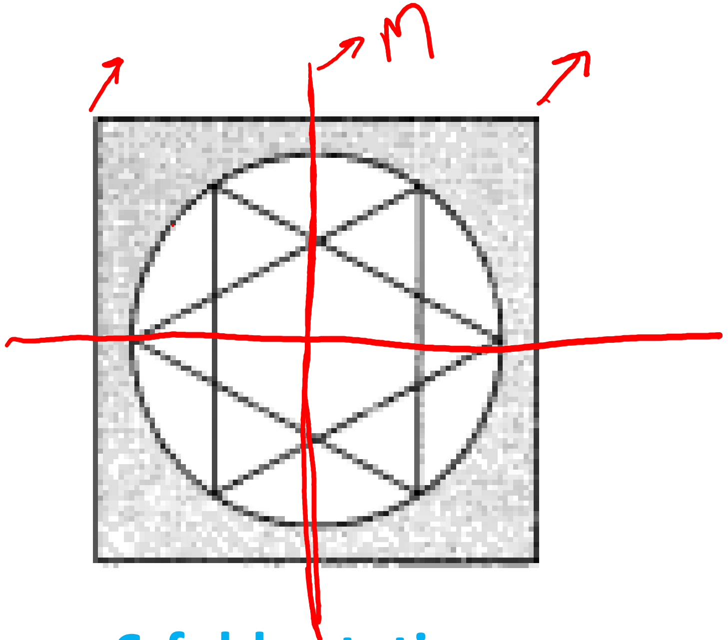
How many alphabets do you think has mirror symmetry along two planes?

H, I, O, X

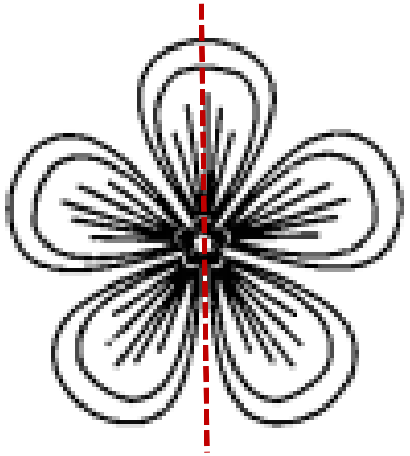
What are the symmetry elements present in these objects?



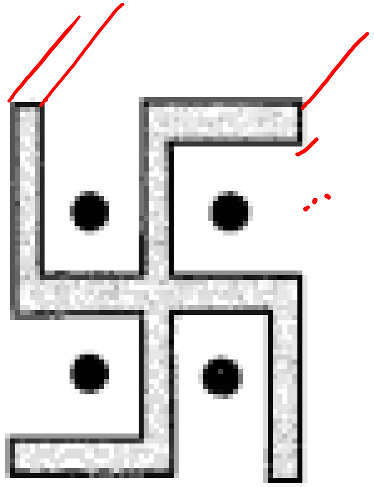
Mirror?



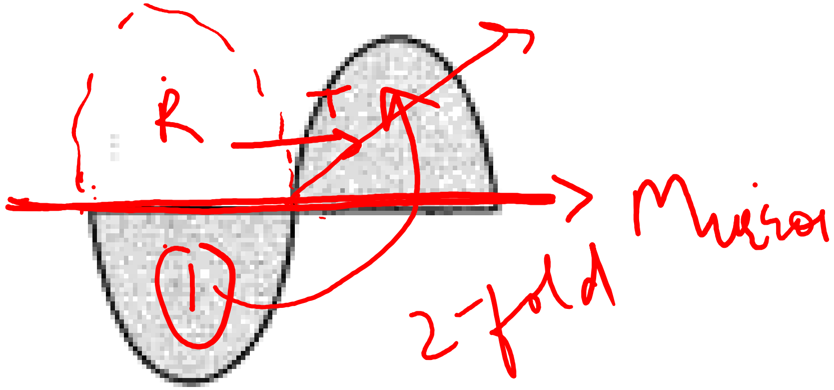
6-fold rotation



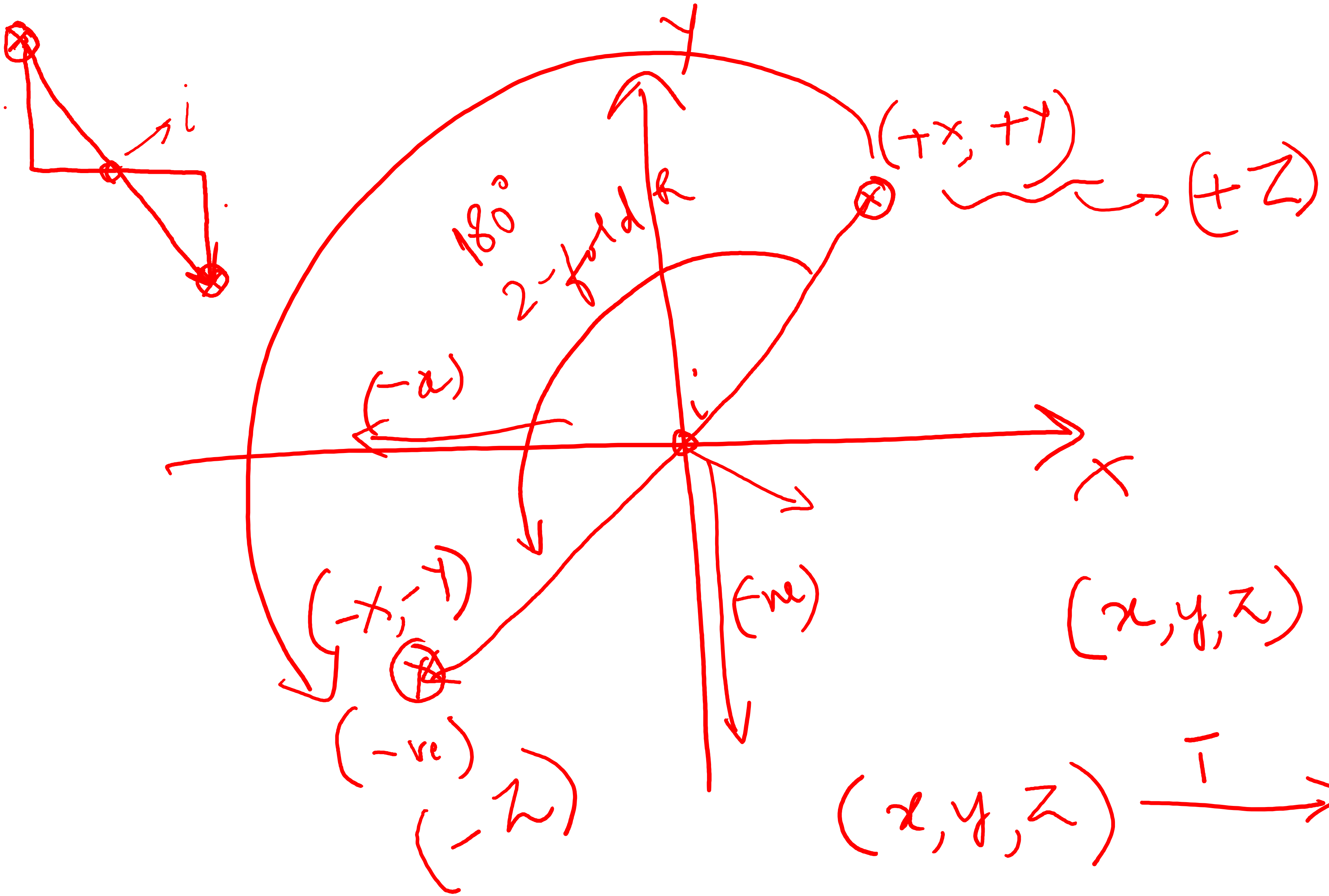
Mirror
5-fold rotation



4-fold rotation
Centre of inversion?



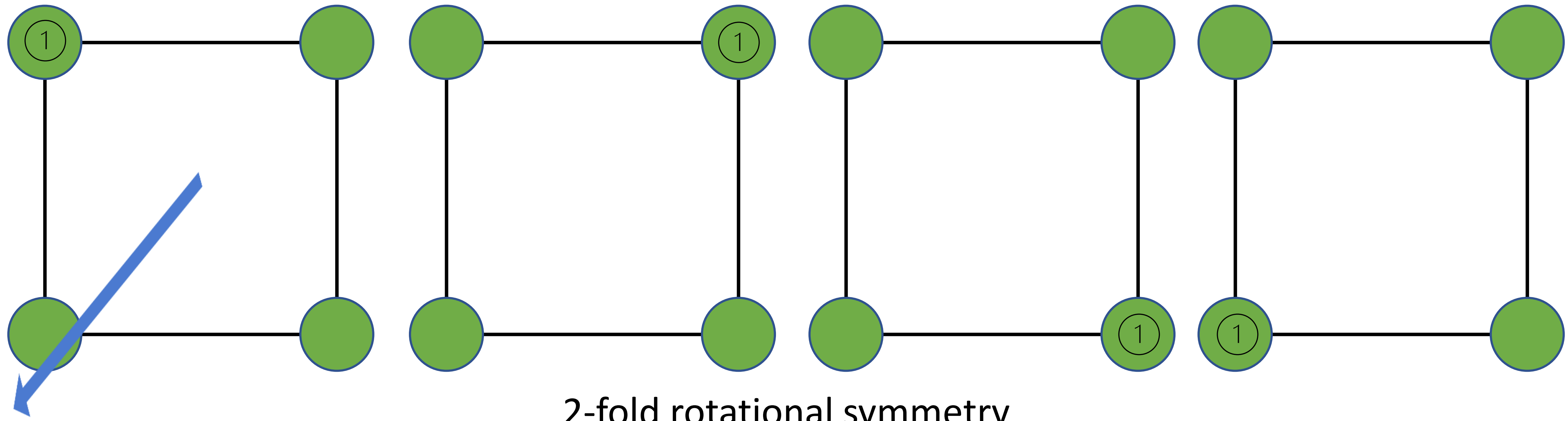
Glide plane



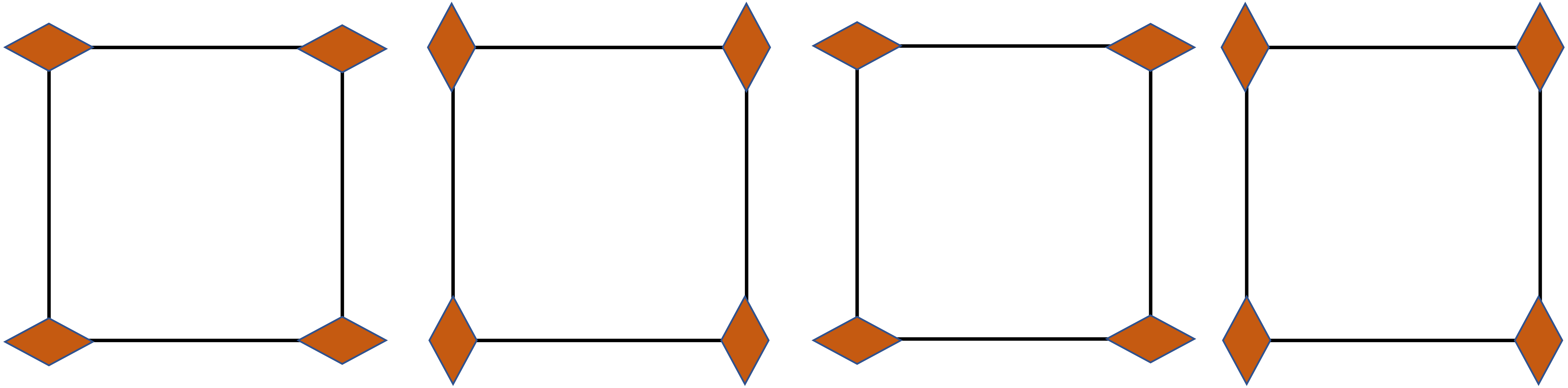
$$(x, y, z) \xrightarrow{2 \parallel z} (-x, -y, z)$$

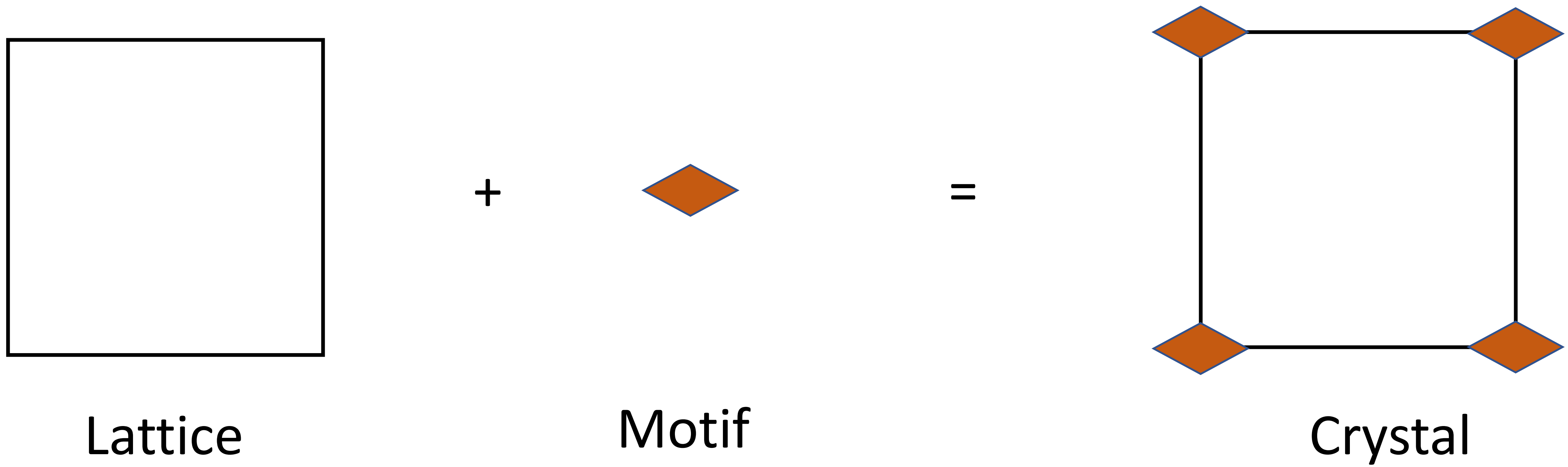
$$(x, y, z) \xrightarrow{\bar{1}} (-x, -y, -z)$$

4-fold rotational symmetry



2-fold rotational symmetry



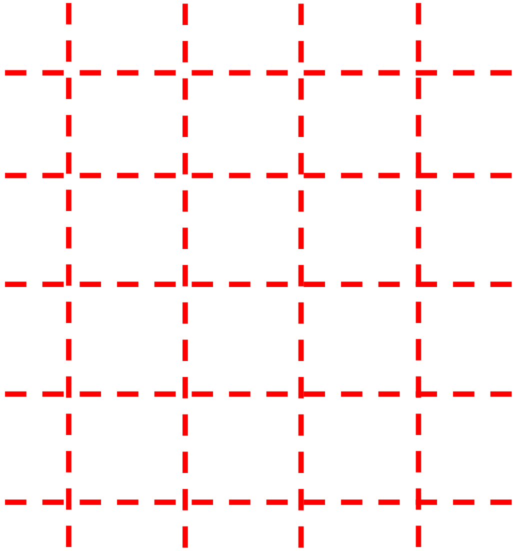


- What factor is likely to govern the symmetry of the crystal?

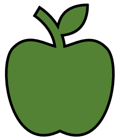
- Symmetry of a crystal will have either equivalent or lower order than that of the symmetry of a lattice.

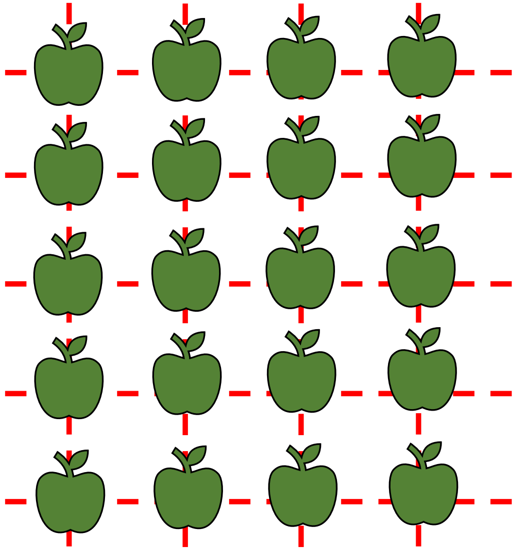
2-D crystal

Lattice **+** **Motif** **=** **Crystal**



\+

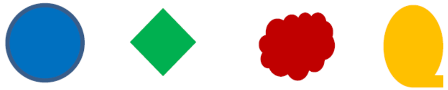




Lattice points: How to repeat?

Translationally periodic arrangement of points

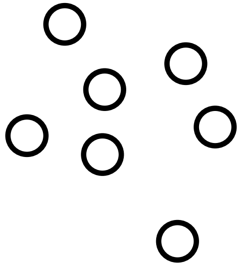
Entity associated with lattice points: What to repeat?



Translationally periodic arrangement of motifs

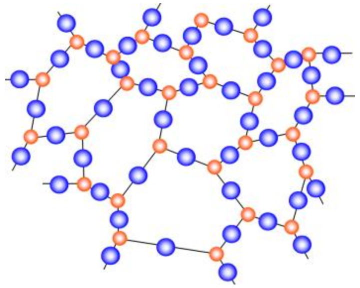
Atomic order of materials

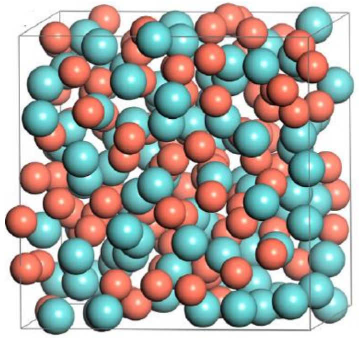
Inert gases (He, Ar)



No regular atomic order

Amorphous
(silicate, metallic glasses)

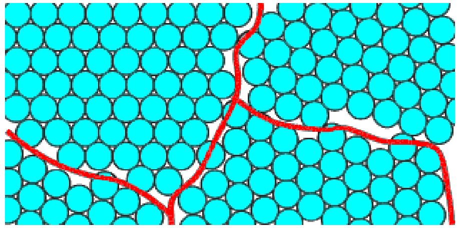




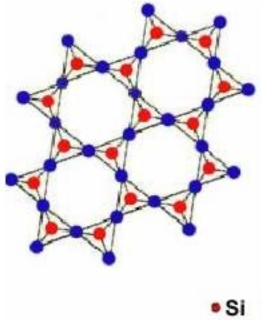
Short-range order;
Lack periodicity in atomic arrangement

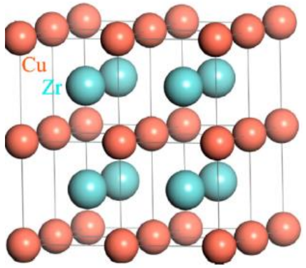
Polycrystal

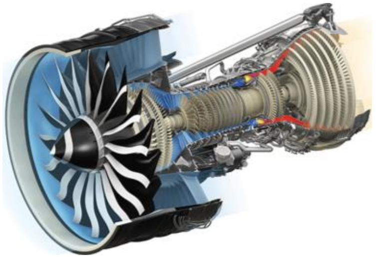
Periodic across each grain



Crystal
(Metals, Ceramics, such as MgO, Al_2O_3; Conductive polymers)







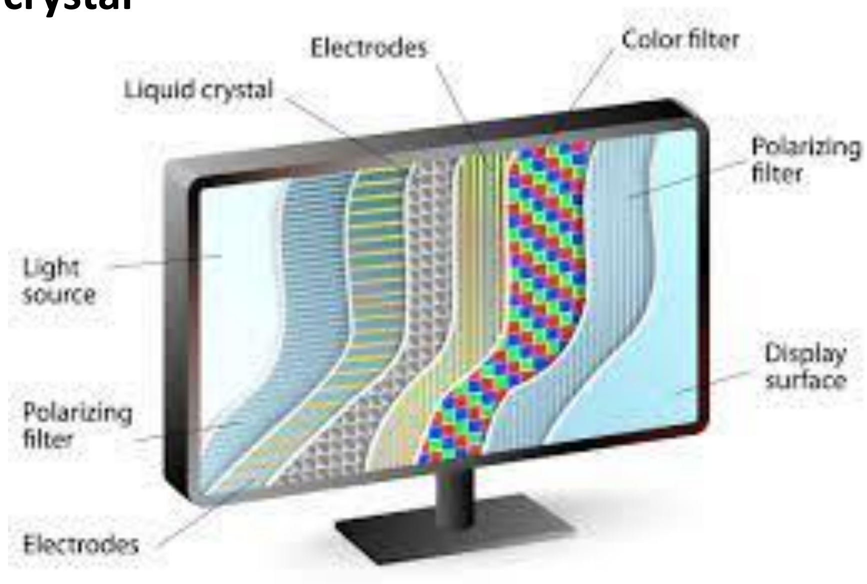
Regular atomic order extending over a large length scale > 100 nm

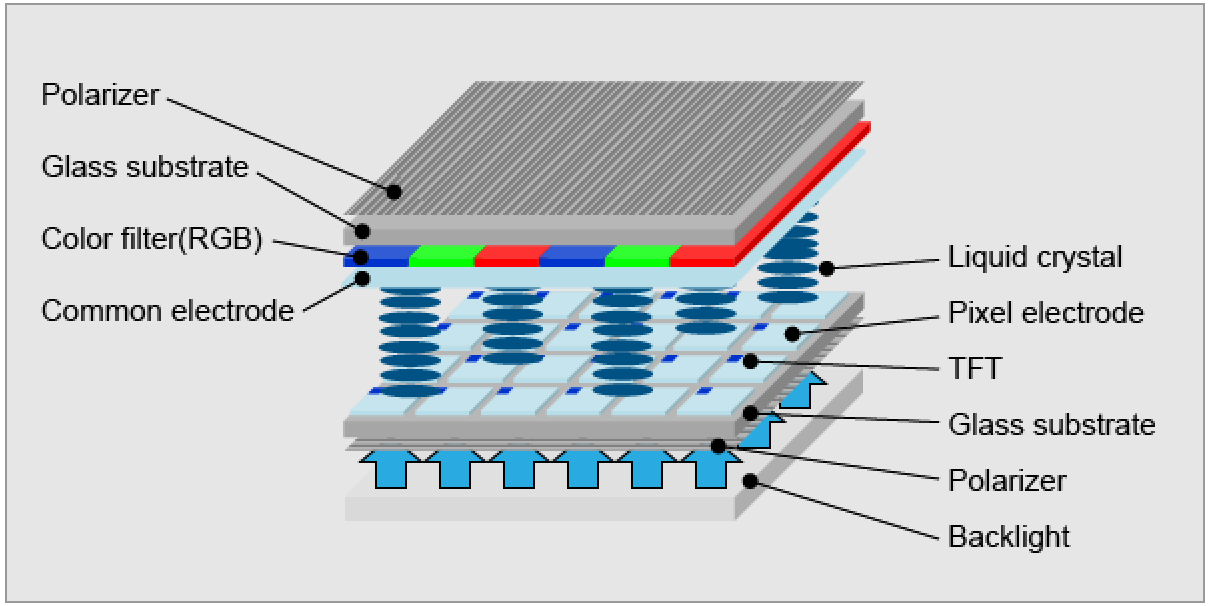
Increase in atomic order

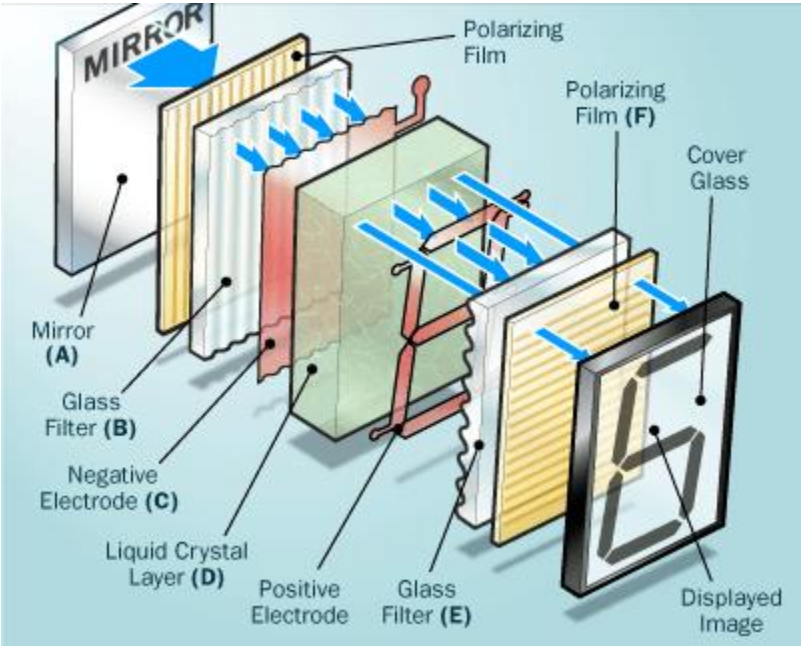
Andrienko J. Molecular Liq. 267 (2018)

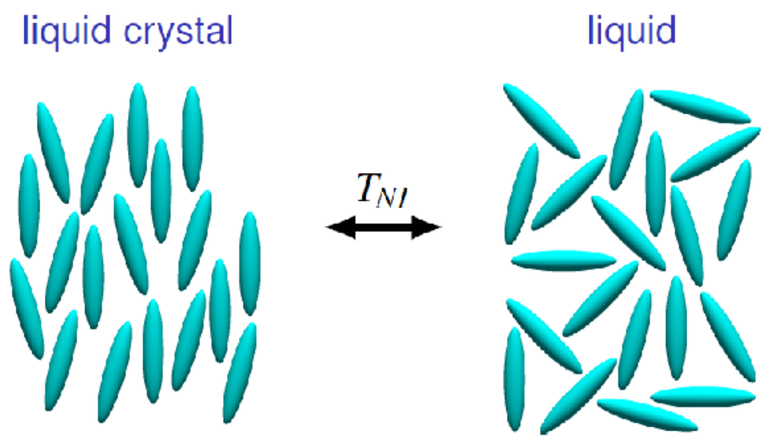
Qiao et al. Mater. Sci. Engg. R 100 (2016)

Liquid crystal



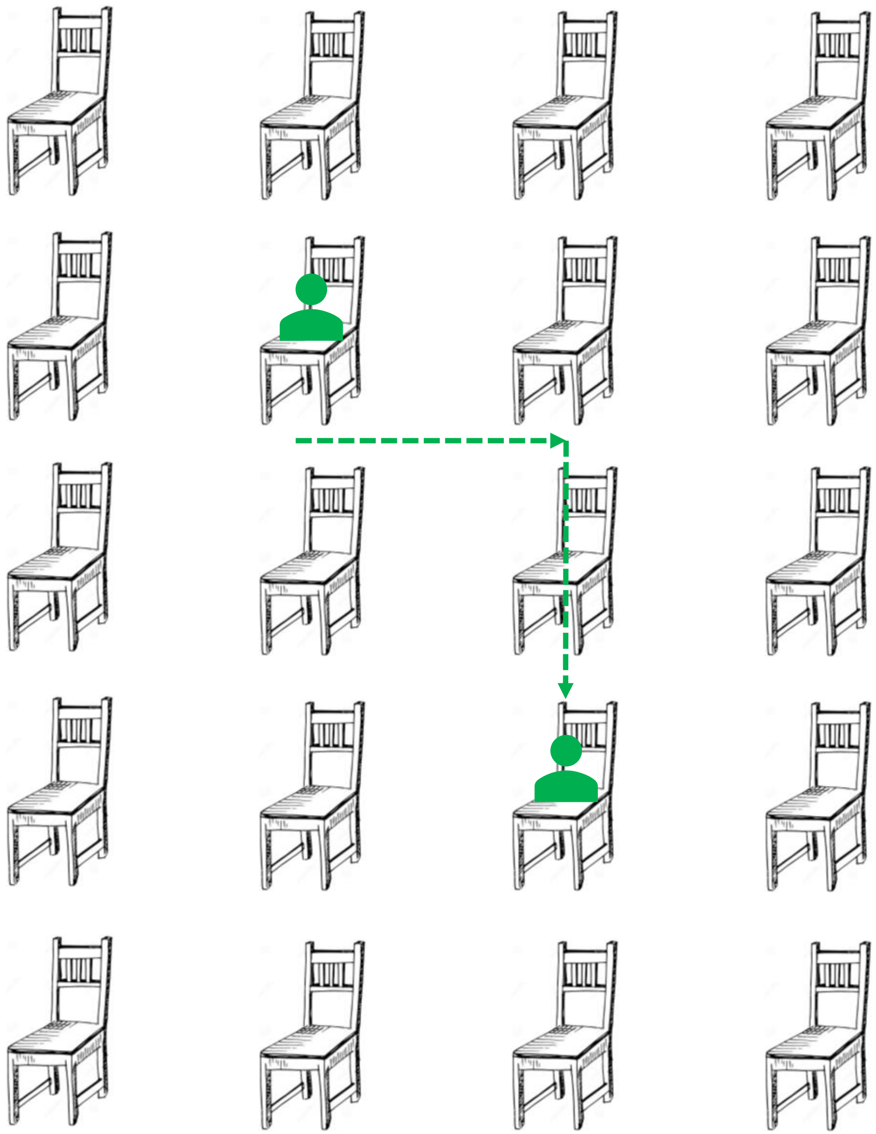






https://www.xenarc.com/lcd-technology.html

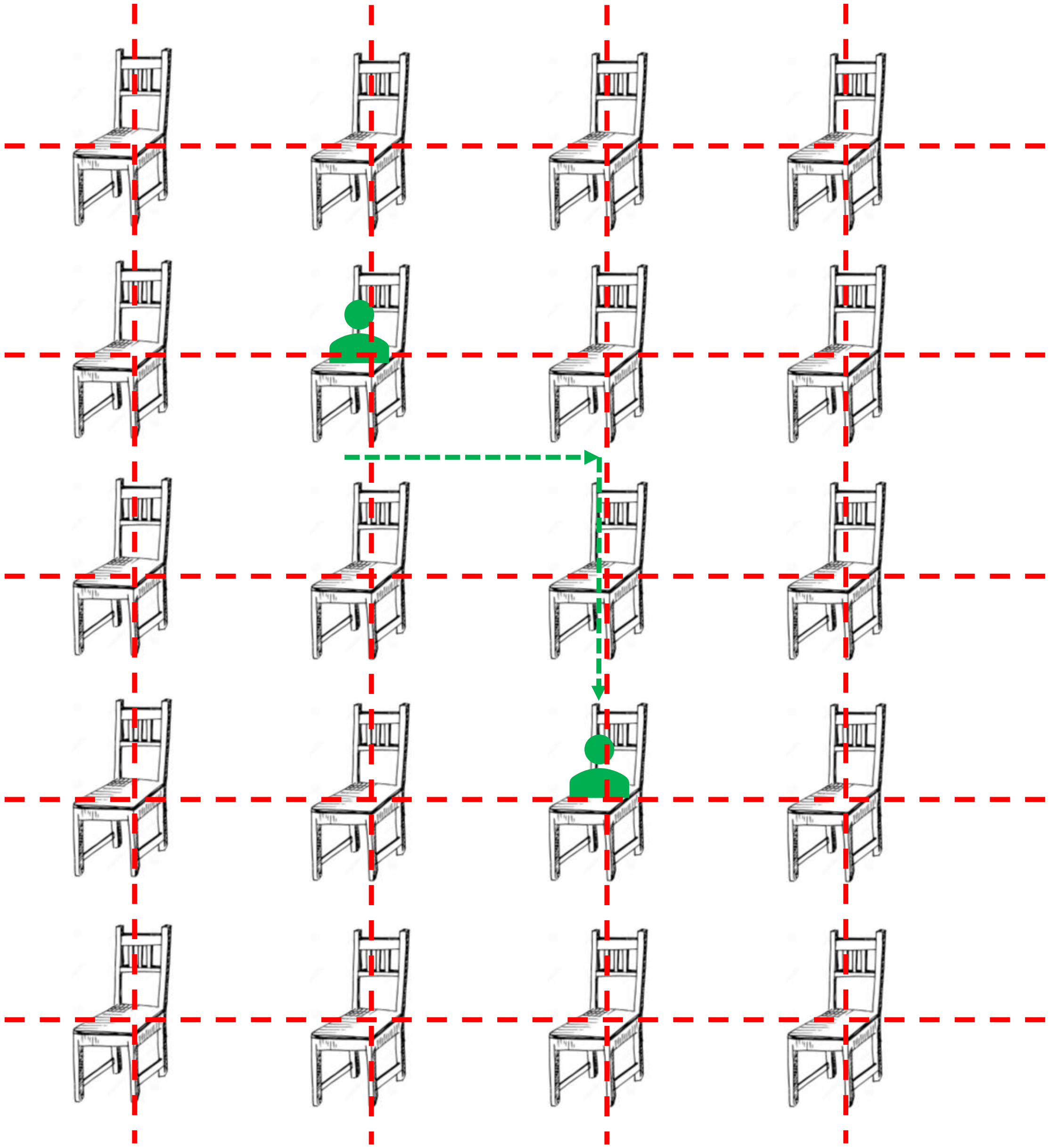
2-D lattice



- Would you be able to make out the difference between your first and second positions looking at its environment?

NO ! ----------→ Both look identical

2-D lattice

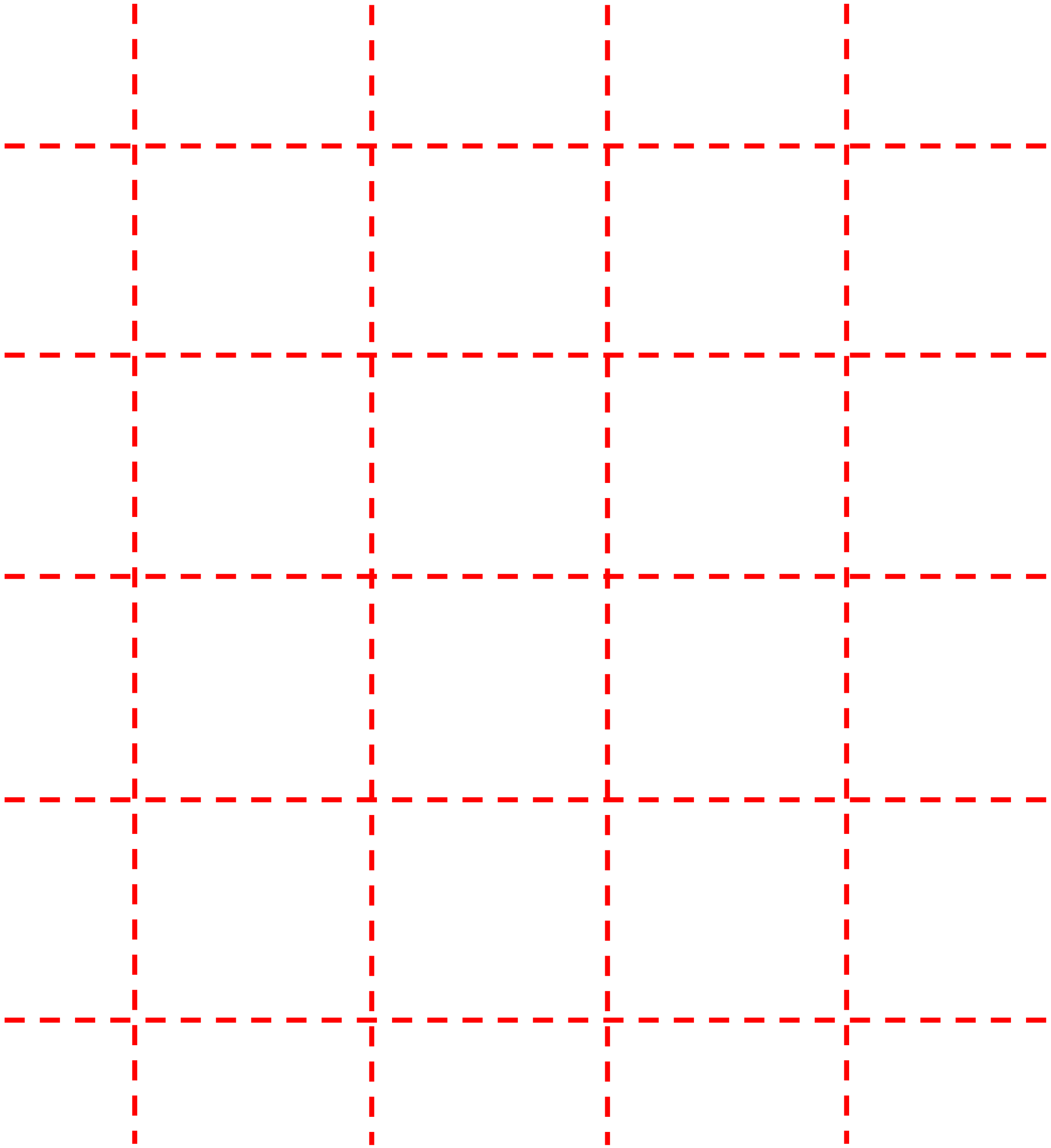


- Would you be able to make out the difference between your first and second positions looking at its environment?

NO ! ----------→ Both look identical

- Translational periodicity

2-D lattice



- Would you be able to make out the difference between your first and second positions looking at its environment?

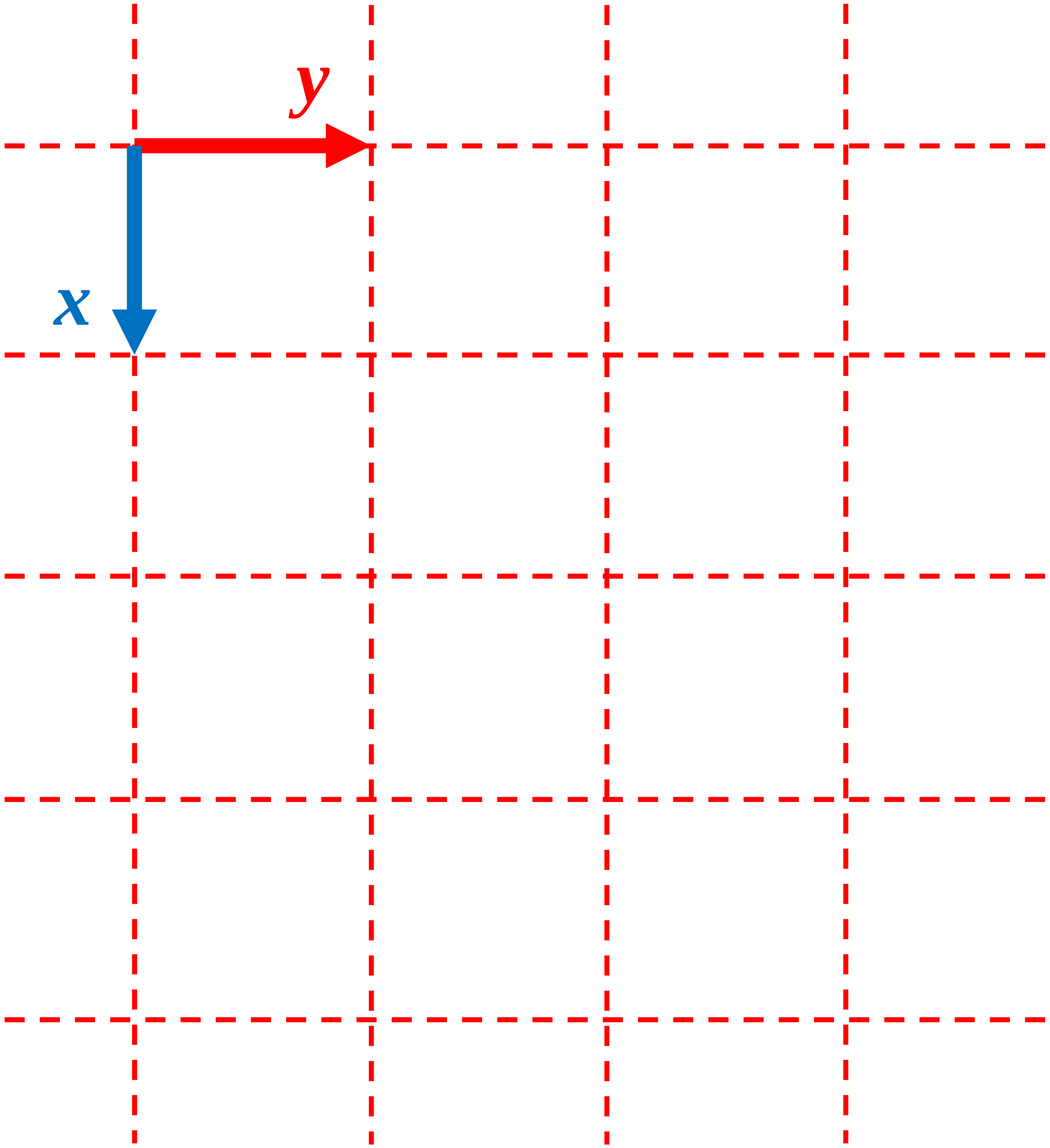
NO ! ----------→ Both look identical

- Translational periodicity

Lattice: Translationally periodic arrangement of points in space such that every point has identical surroundings

- **Dotted grid is a 2-D Square lattice and the intersection points are called the lattice points**

2-D square lattice



- Would you be able to make out the difference between your first and second positions looking at its environment?

NO ! ----------→ Both look identical

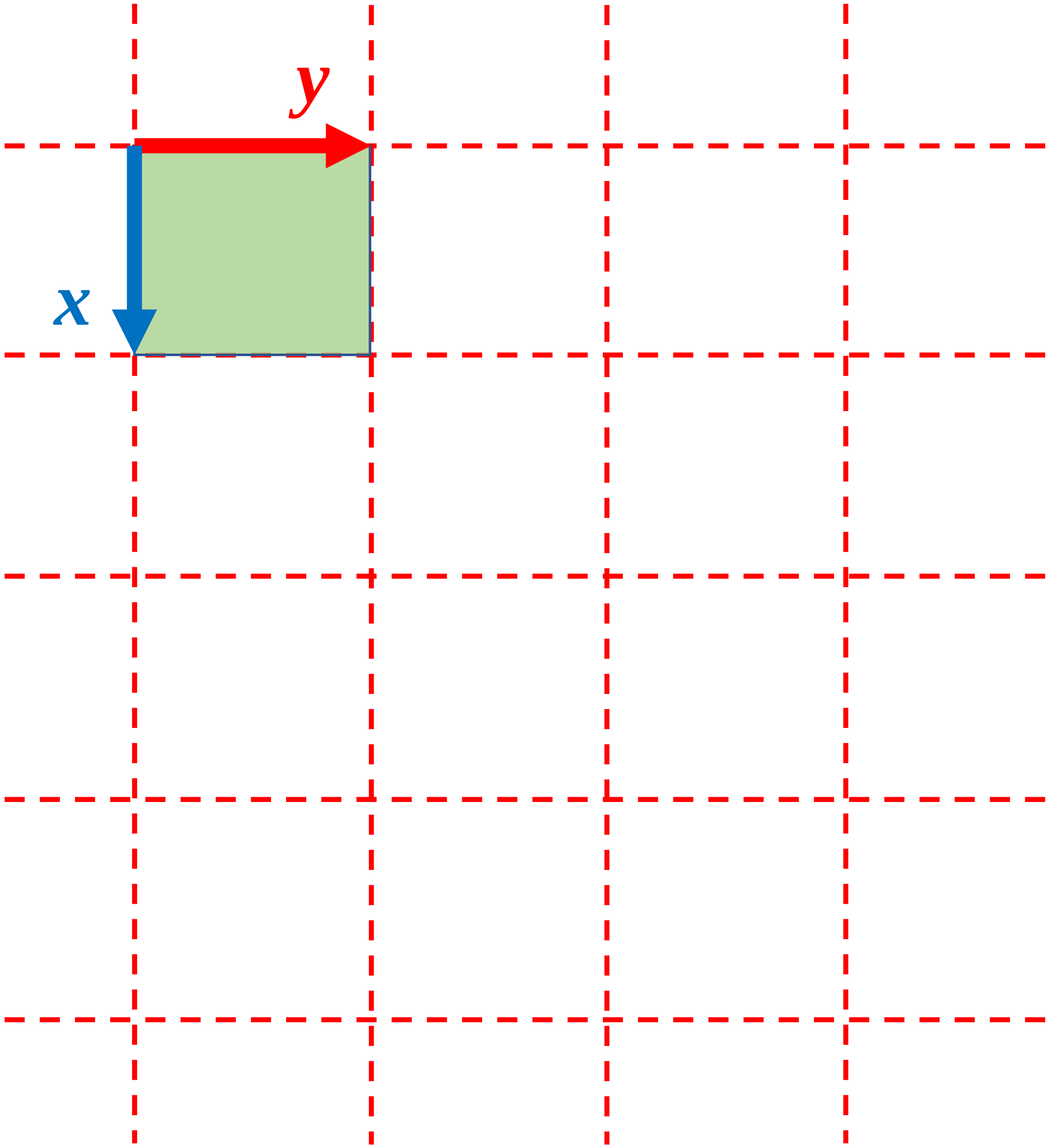
- Translational periodicity

Lattice: Translationally periodic arrangement of points in space such that every point has identical surroundings

- **Dotted grid is a 2-D Square lattice and the intersection points are called the lattice points**

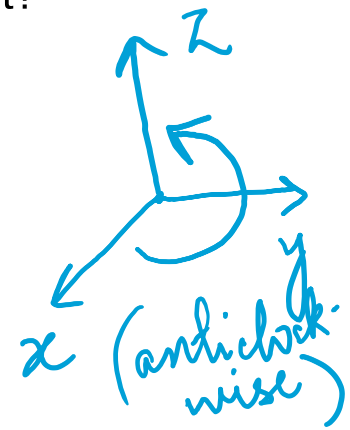
- Translational lattice/basis vectors

2-D square lattice



- Would you be able to make out the difference between your first and second positions looking at its environment?

NO ! ----------→ Both look identical

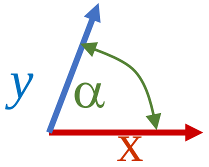


- Translational periodicity

Lattice: Translationally periodic arrangement of points in space such that every point has identical surroundings

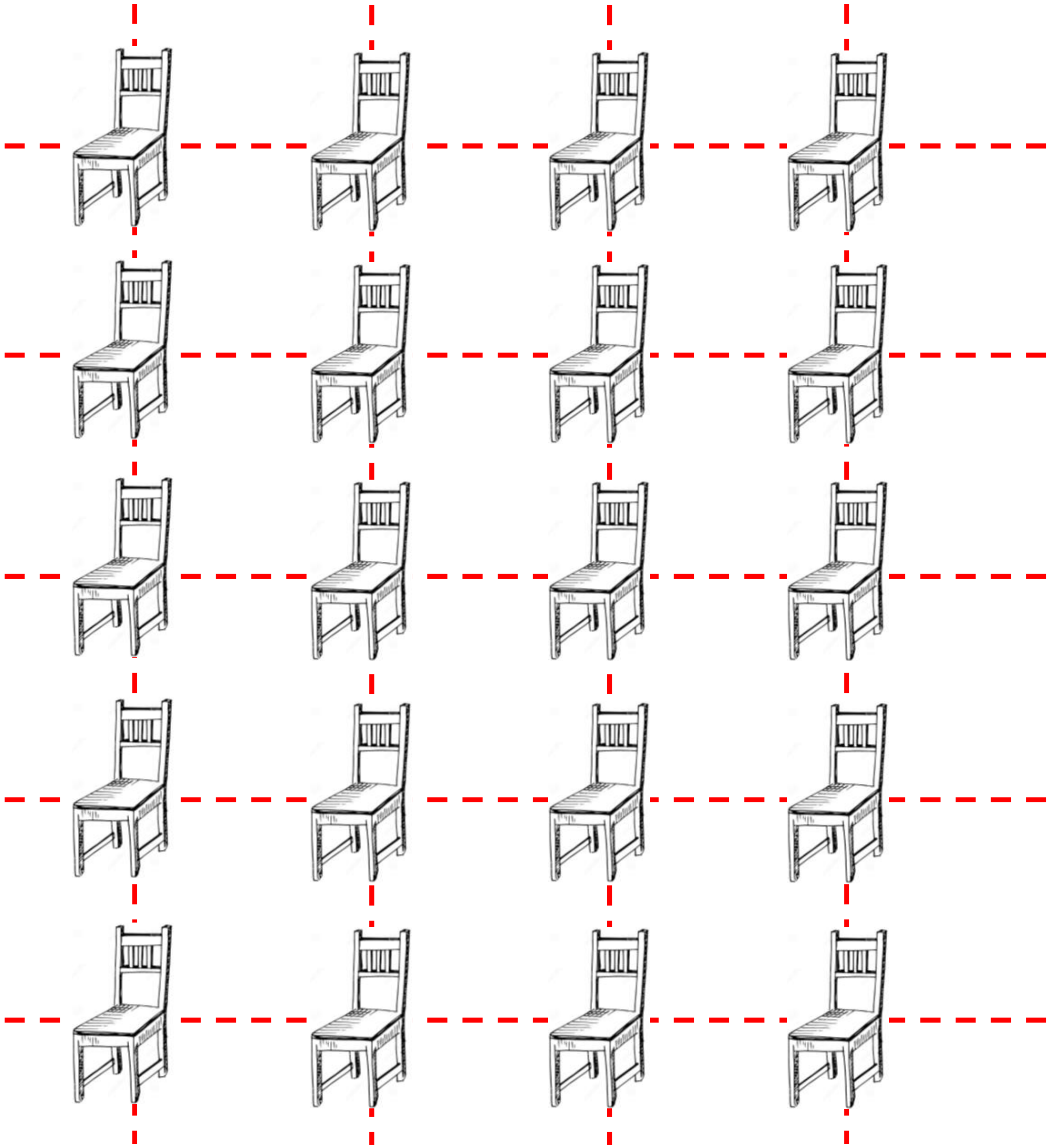
- **Dotted grid is a 2-D Square lattice and the intersection points are called the lattice points**

- Translational lattice/basis vectors



- **Unit cell** : Smallest area enclosed by the lattice vectors

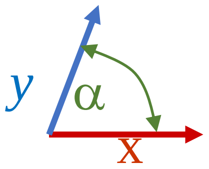
Motif



Lattice: Translationally periodic arrangement of points in space such that every point has identical surroundings

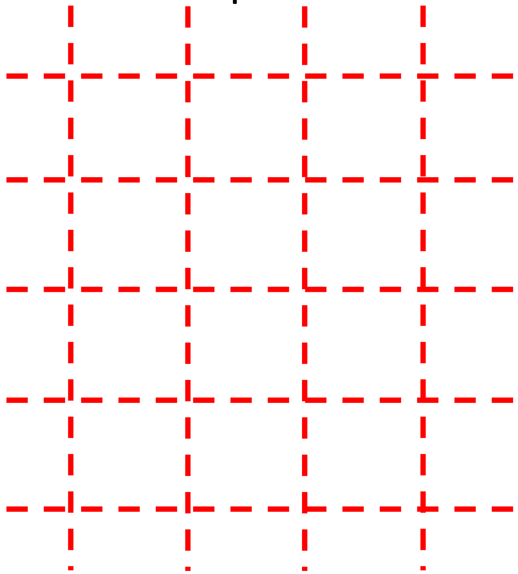
- **Dotted grid is a 2-D Square lattice and the intersection points are called the lattice points**

Entity associated with the lattice point is called a **motif**

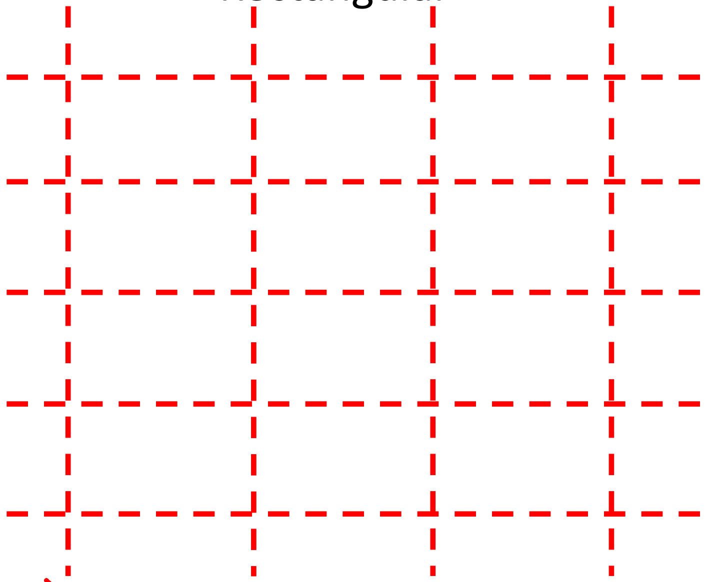


2-D lattice

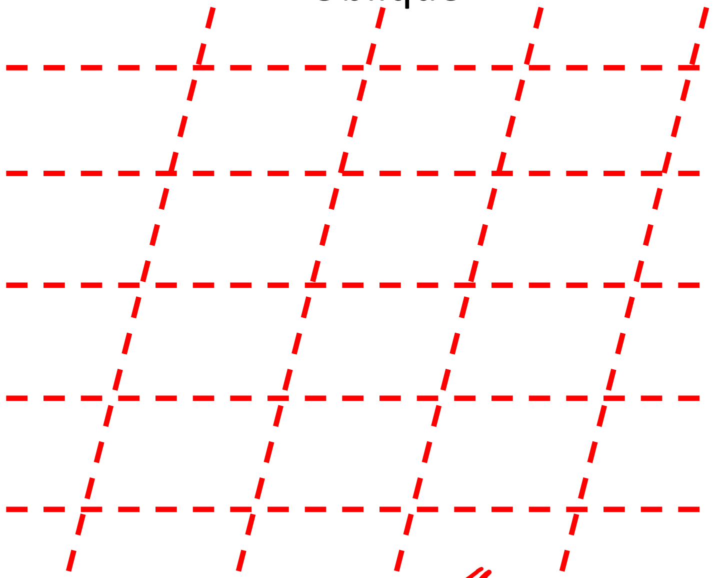
Square



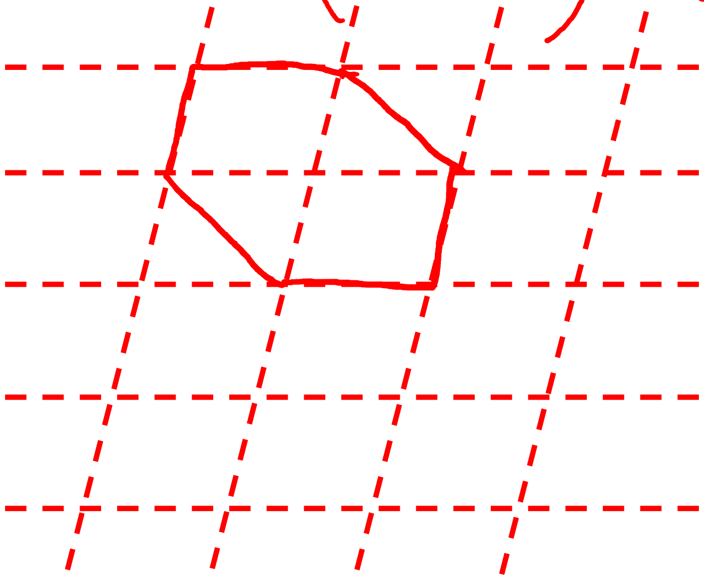
Rectangular

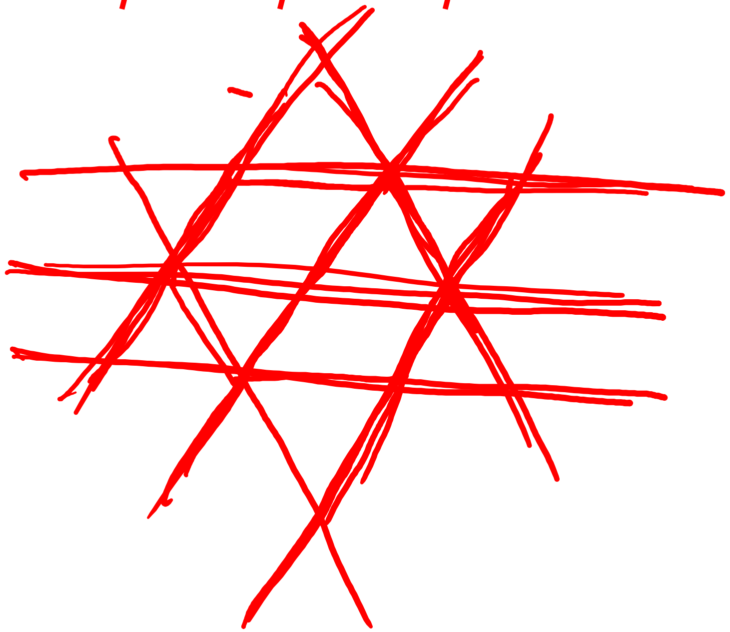


Oblique



(Hexagonal) → Square Oblique.





MLL 100

Introduction to Materials Science and Engineering

Lecture-3

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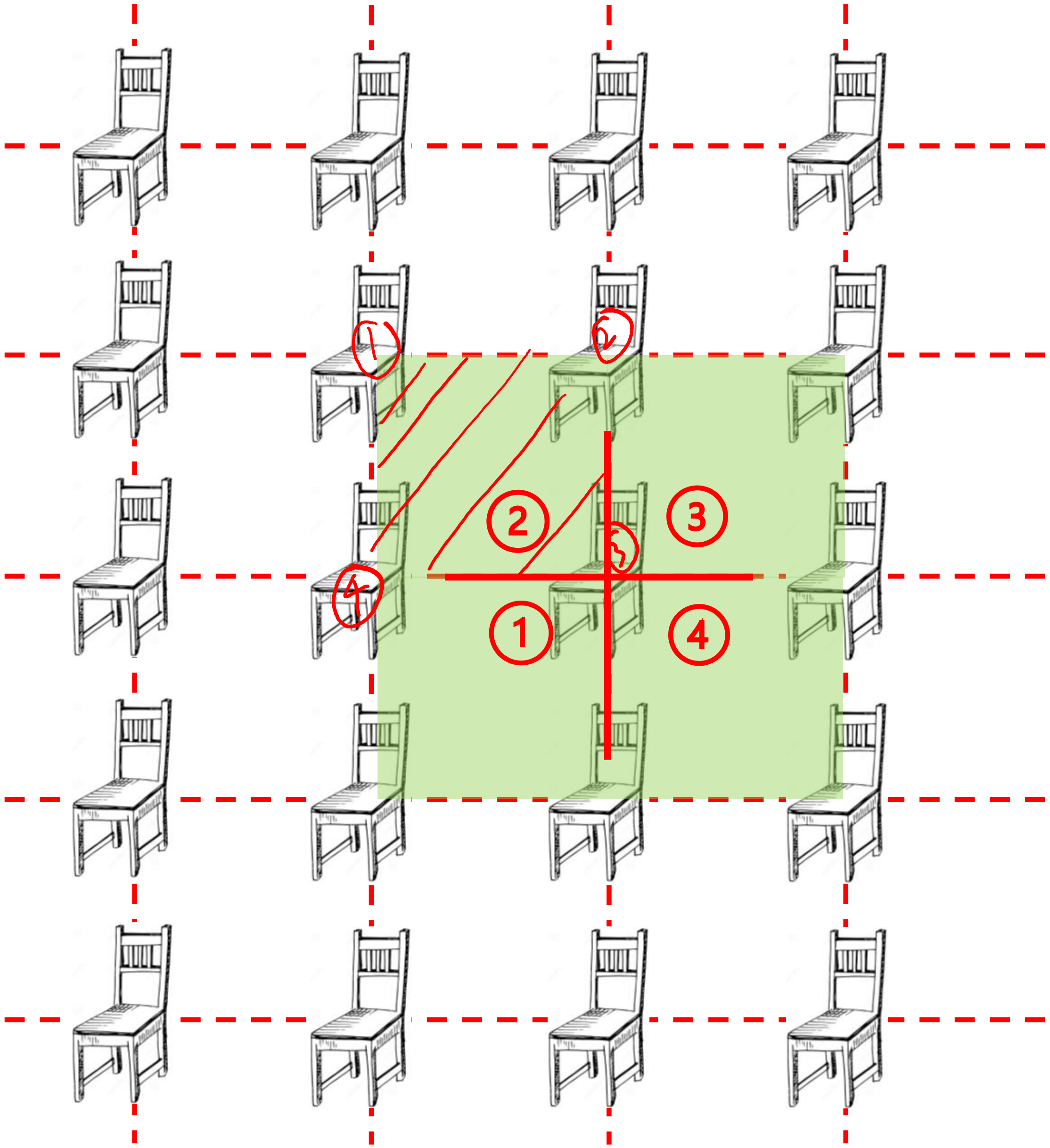
IIT Delhi
Department of Materials Science and Engineering

January 07, 2022

What we learnt in Lecture-2?

- Symmetry operations: Inversion, Glide
- Lattice, Motif
- Classification of materials: atomic order

Primitive and non-primitive cell



Lattice: Translationally periodic arrangement of points in space such that every point has identical surroundings

- **Dotted grid is a 2-D Square lattice and the intersection points are called the lattice points**

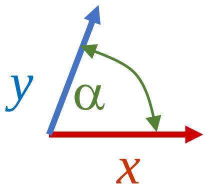
Entity associated with the lattice point is called a **motif**

- **How many chairs per unit cell?**

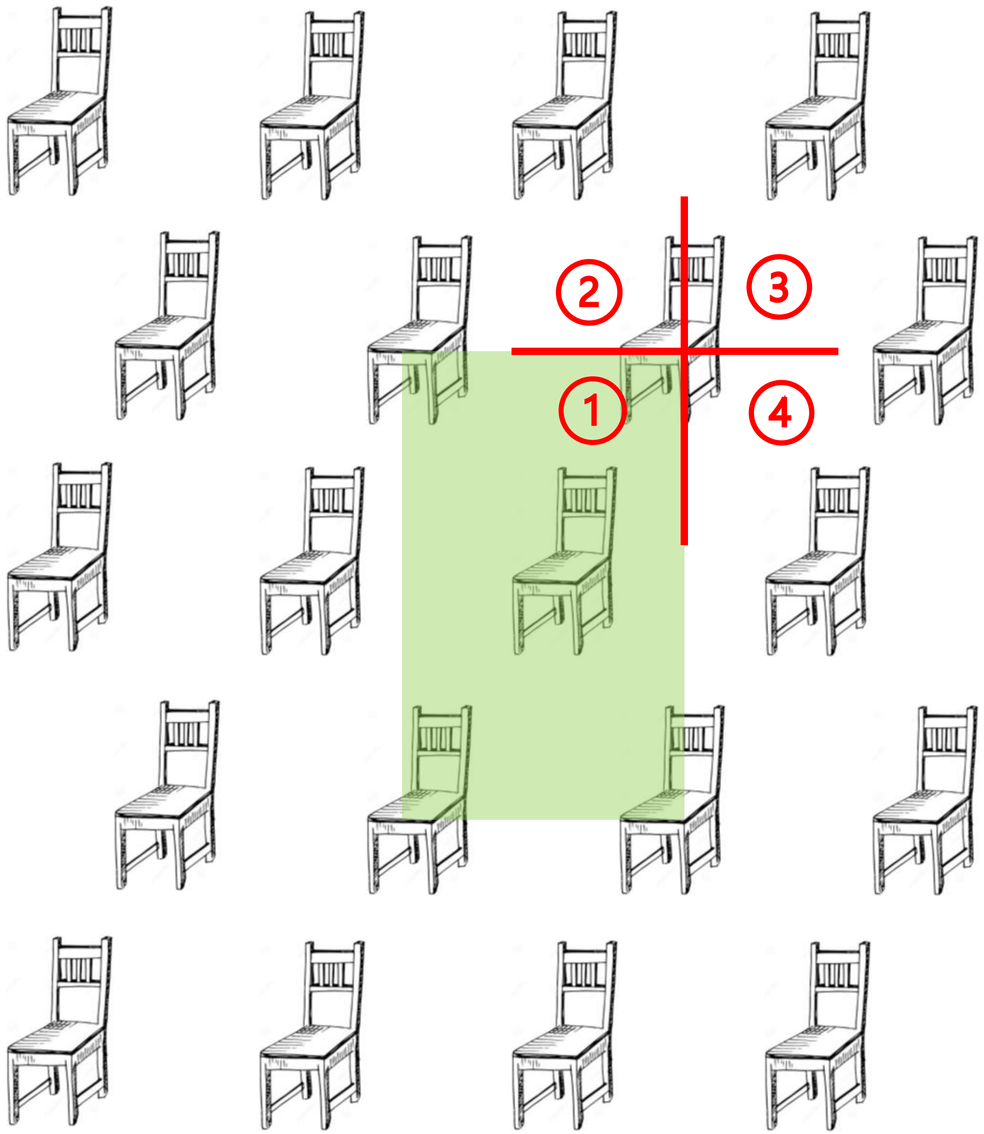
One $\left(\frac{1}{4}\right)^{th}$ → Each chair

Total chairs = 4

$\left(4 \times \frac{1}{4}\right) = 1$

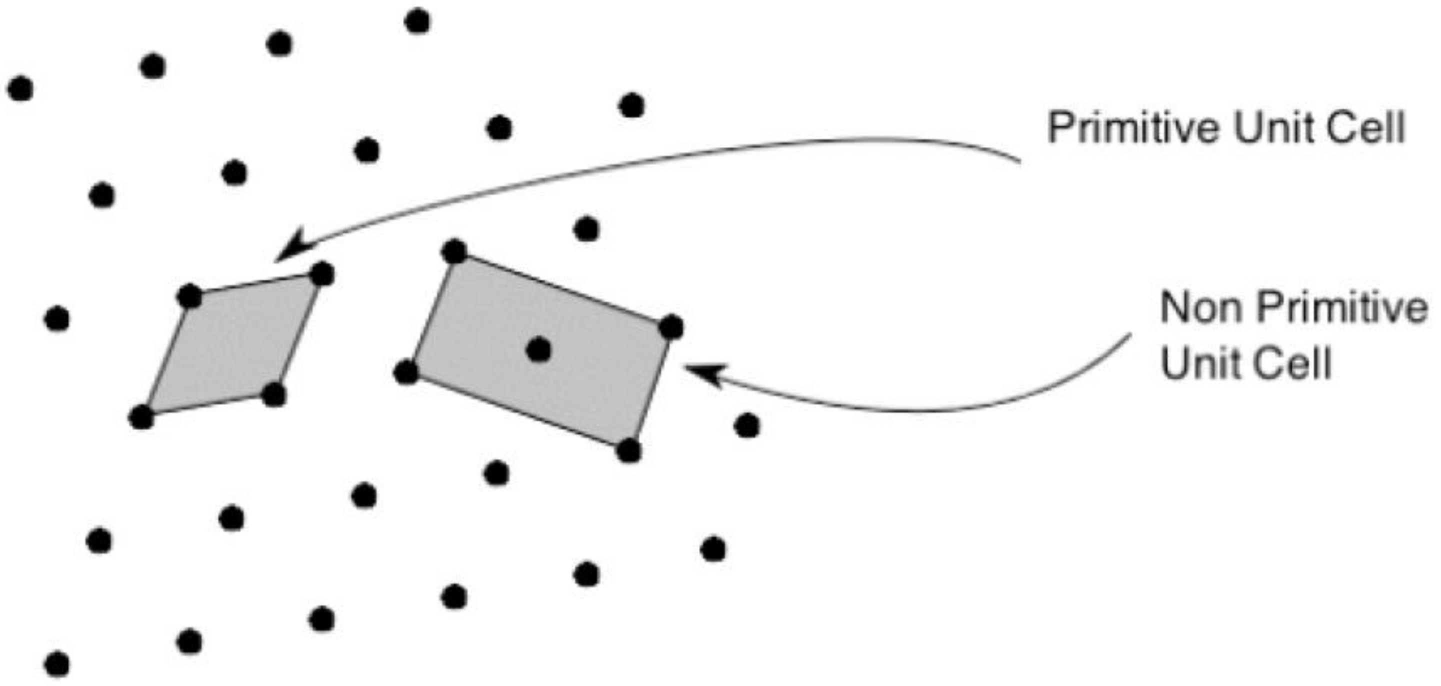


Primitive and non-primitive cell



- **How many chairs per unit cell?**

  Two



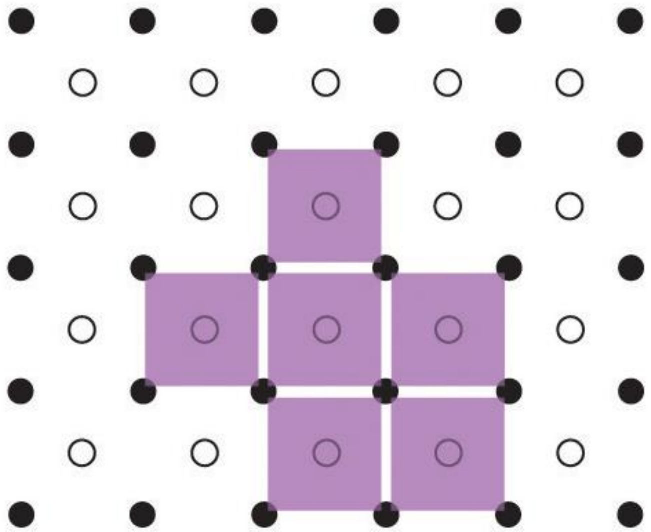
Primitive unit cell:

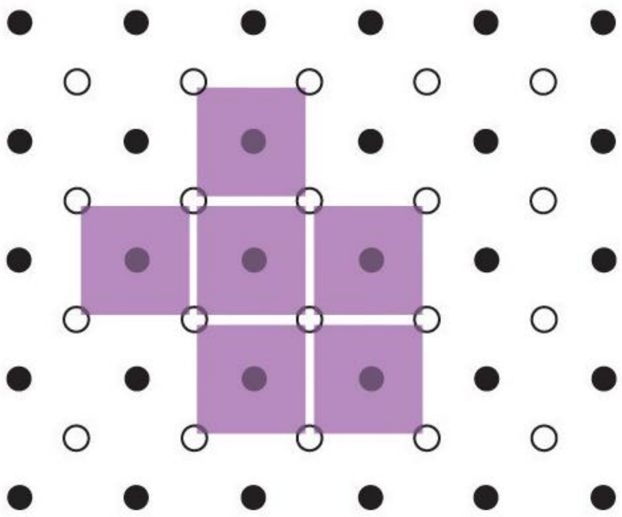
Only one lattice point, made up from the lattice points at each of the corners.

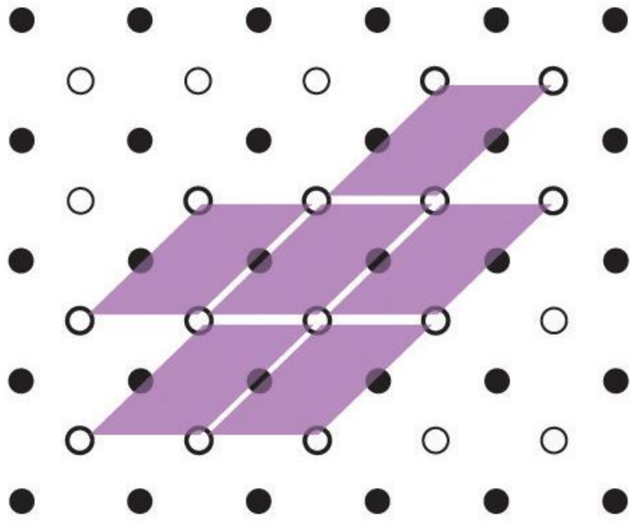
Non-primitive unit cell:

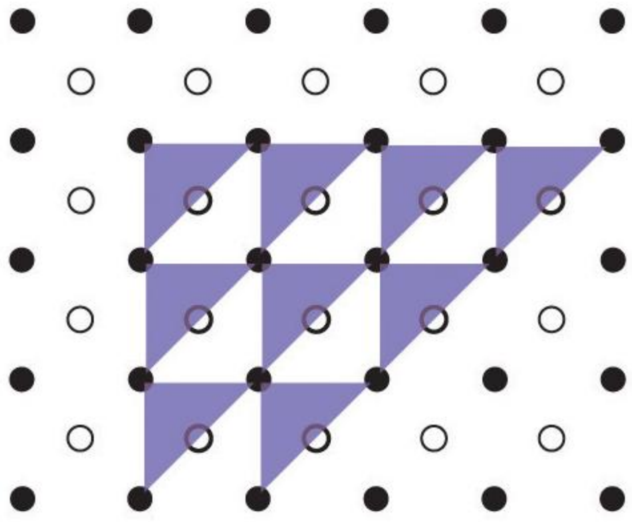
Additional lattice points, either on a face or edge or within, and therefore, have more than one lattice point per unit cell.

Number of lattice points per unit cell









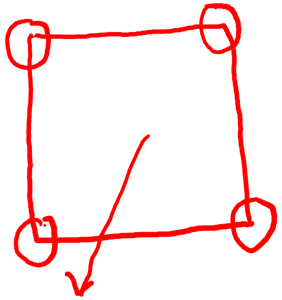
What are the factors governing the selection of my lattice?

- Should enclose smallest possible area
- Symmetry of the lattice should be higher

Centered square lattice = Simple square lattice

2-D lattices

Lattice	Symmetry	Shape of UC	Lattice Parameters
Square	4mm	Square	$(a = b\ ,\ \alpha = 90°)$
Rectangle	mm2	Rectangle	$(a \neq b,\ \alpha = 90°)$
Centered Rectangle	**mm2**	Rectangle	$(a \neq b,\ \alpha = 90°)$
Hexagonal	6mm	120° Rhombus	$(a = b,\ \alpha = 120°)$
Rectangular Oblique	2	Parallelogram	$(a \neq b,\ \alpha$ general value)



4-fold ∥ z

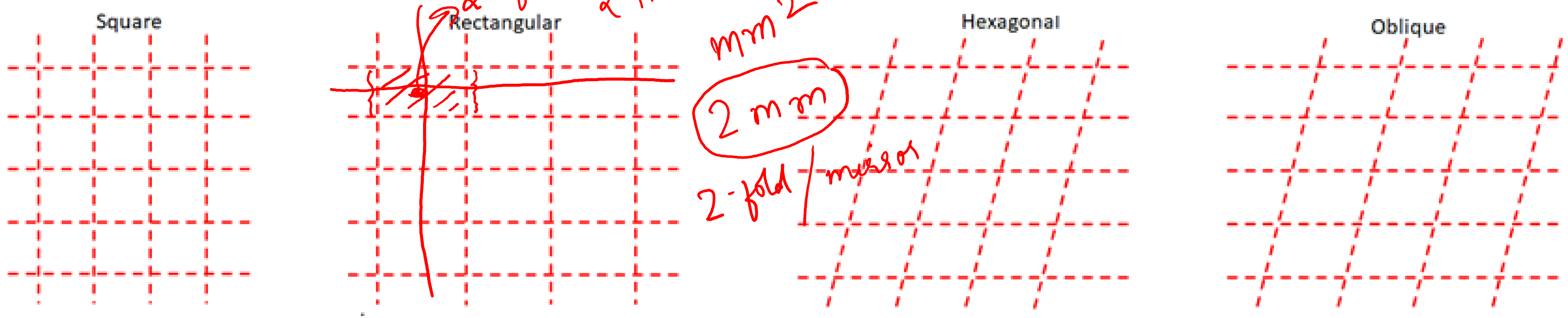
4mm → m ⊥ y
→ m ⊥ x
4 ∥ z

2-fold.
2 ∥ z

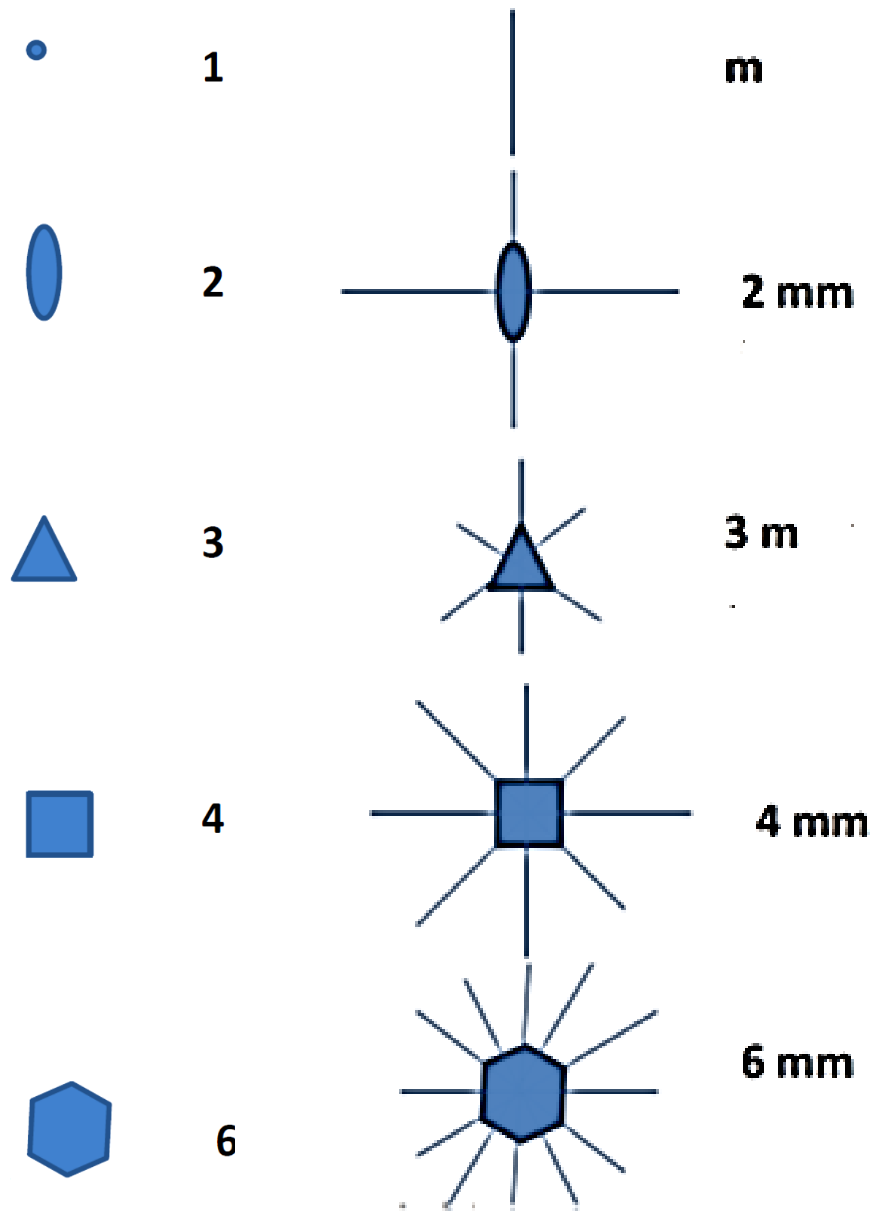
mm2

2mm

2-fold / mirror



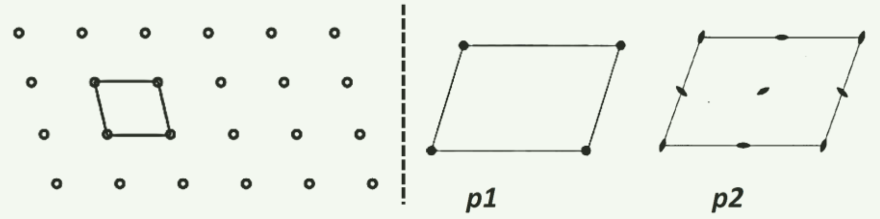
10 point groups + 5 2-D lattice = 17 plane groups



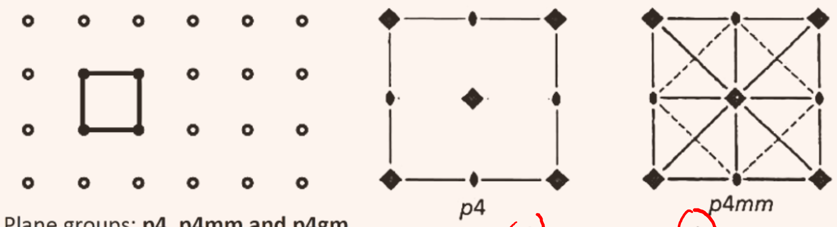
Square
Rectangle
Centered Rectangle
Hexagonal
Rectangular Oblique

17 Plane groups

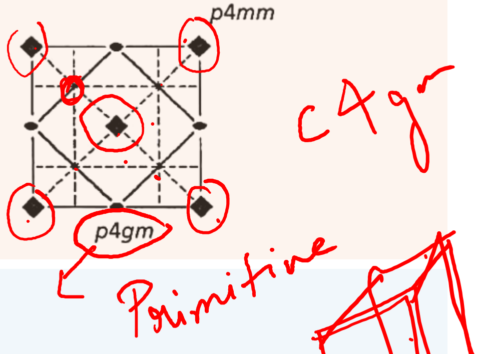
Oblique (parallelogram) (a ≠ b, ≠ 90°)



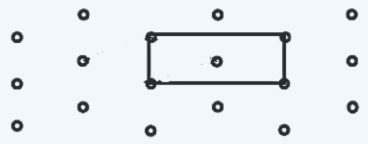
Square (a = b, 90°)

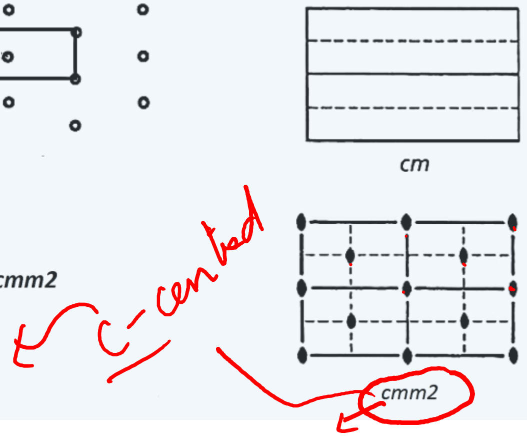


Plane groups: **p4, p4mm and p4gm**



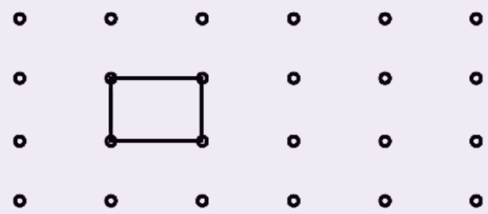
Centered rectangular (a ≠ b, 90°)

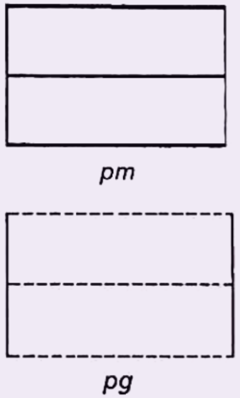




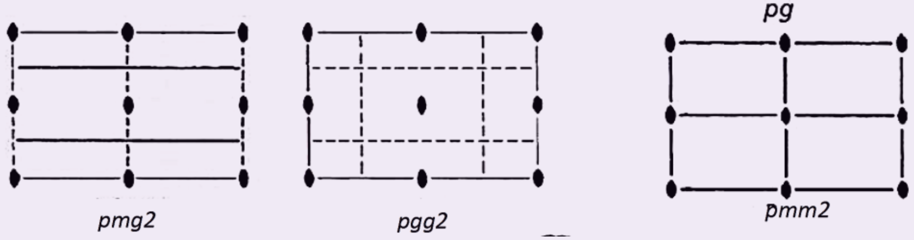
Plane groups: *cm* and *cmm2*

Rectangular (a ≠ b, 90°)

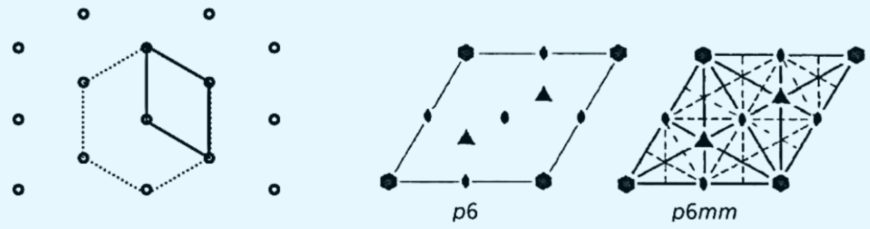




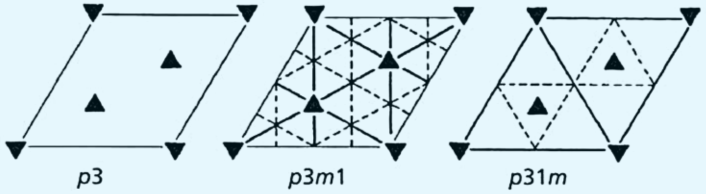
Plane groups: *pm, pg, pmg2, pmm2* and *pgg2*



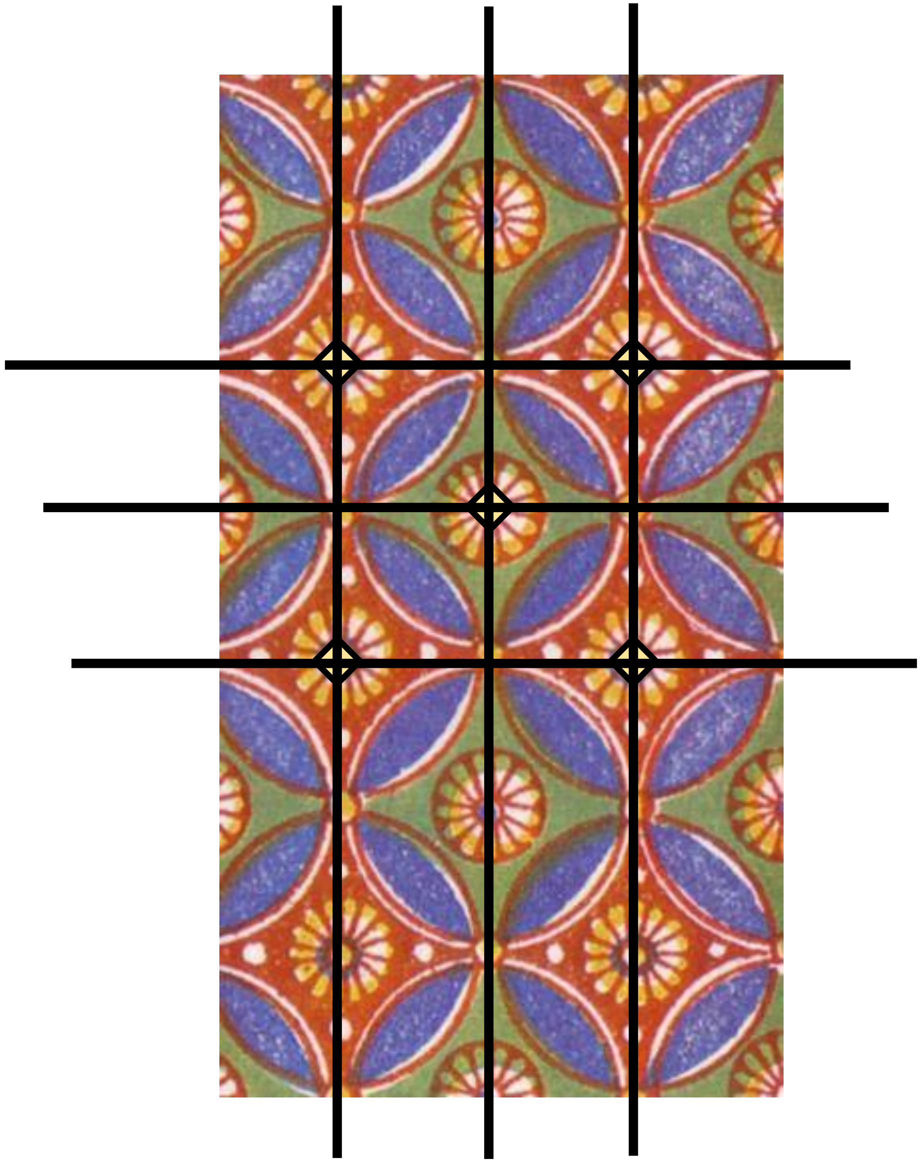
Rhombic or hexagonal (a = b, 120°)



Plane groups:
p3, p31m, p3m1, p6 and p6mm



What does the 'g' stand for?

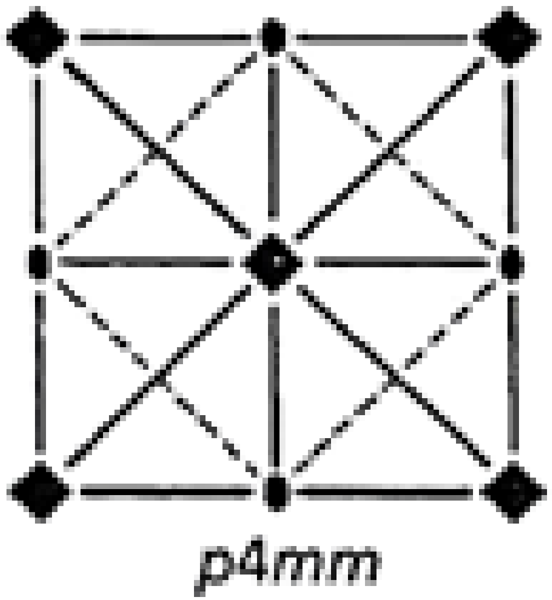


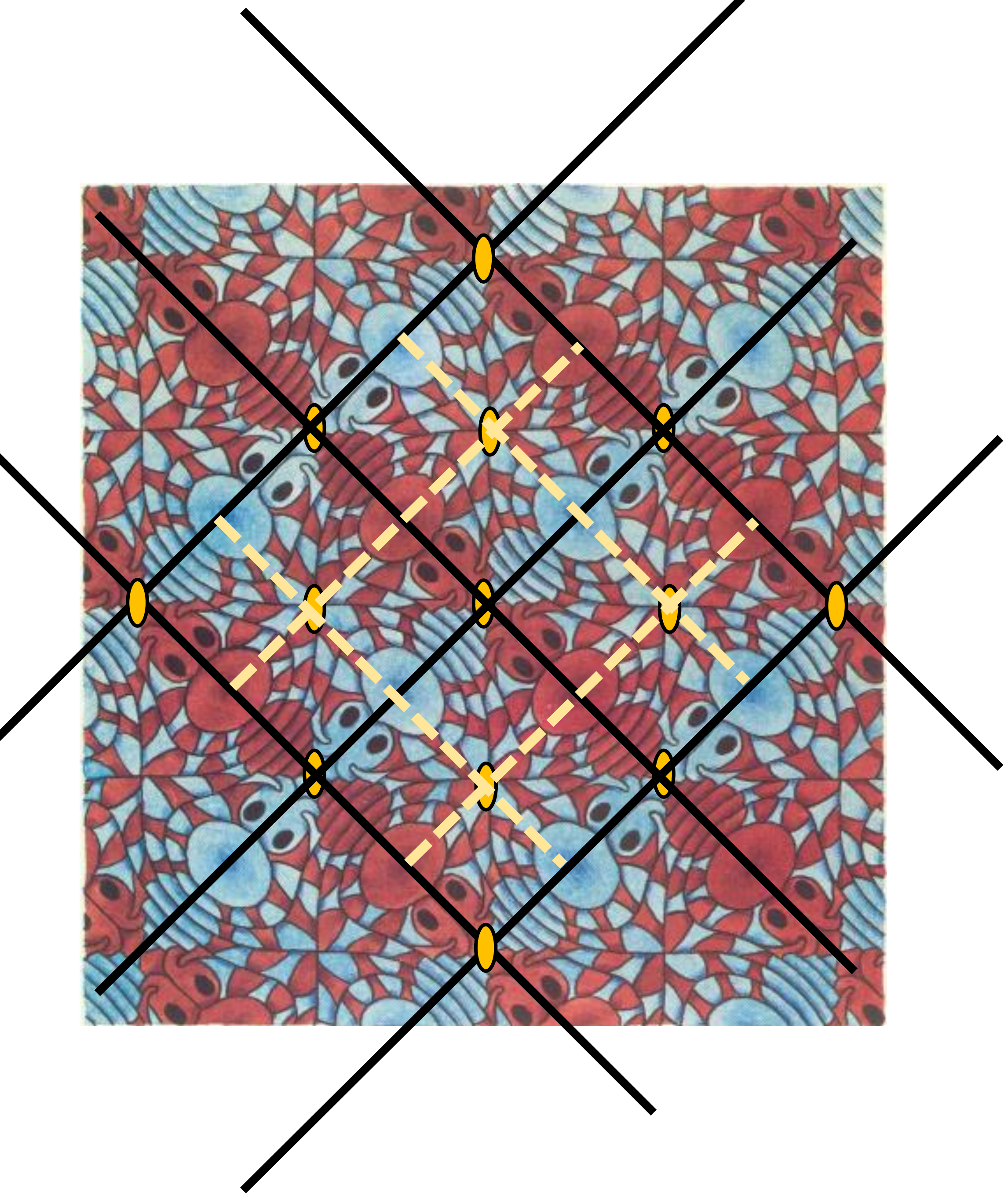
- What is the highest symmetry of rotation?

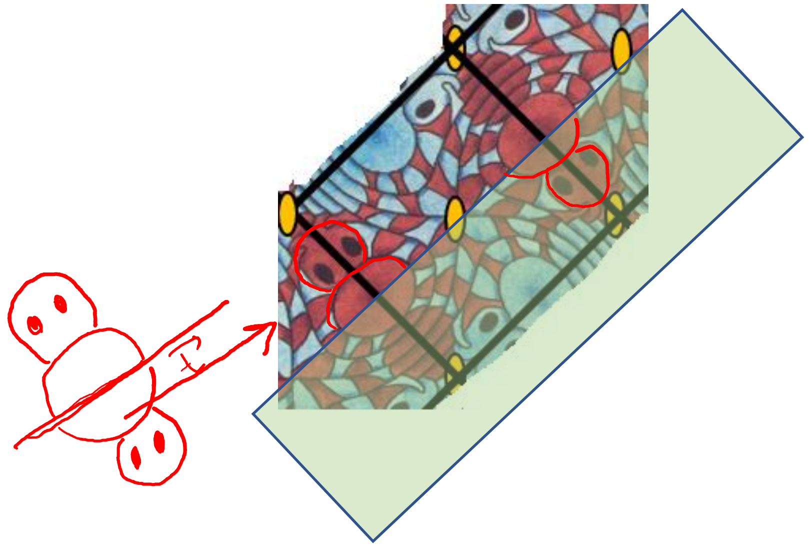
4-fold II z

- Is mirror (m) present perpendicular to any of the axes?

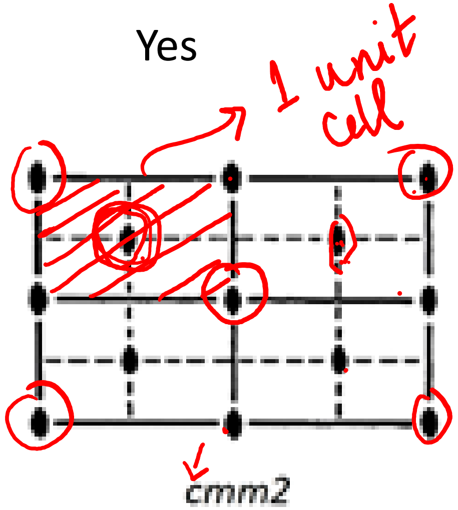
Yes, m







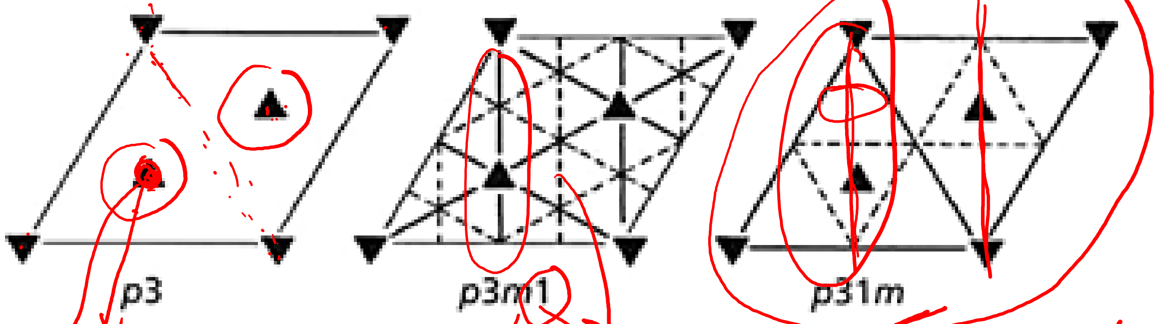
- What is the highest symmetry of rotation? 2-fold II z
- Is mirror (m) present perpendicular to any of the axes? Yes, m
- Are the mirrors perpendicular to each other? Yes



17 PG

p3mm
p3m2

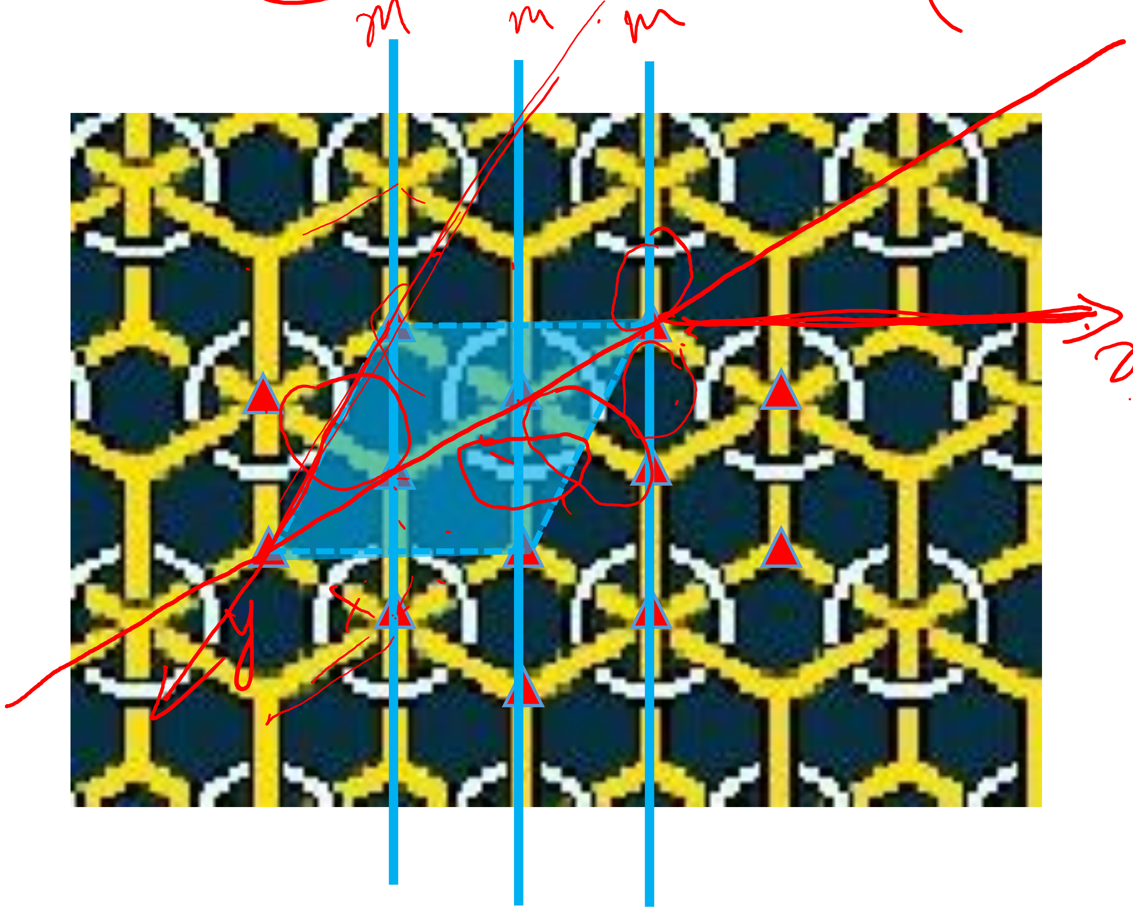
Bold solid
(Mirror)

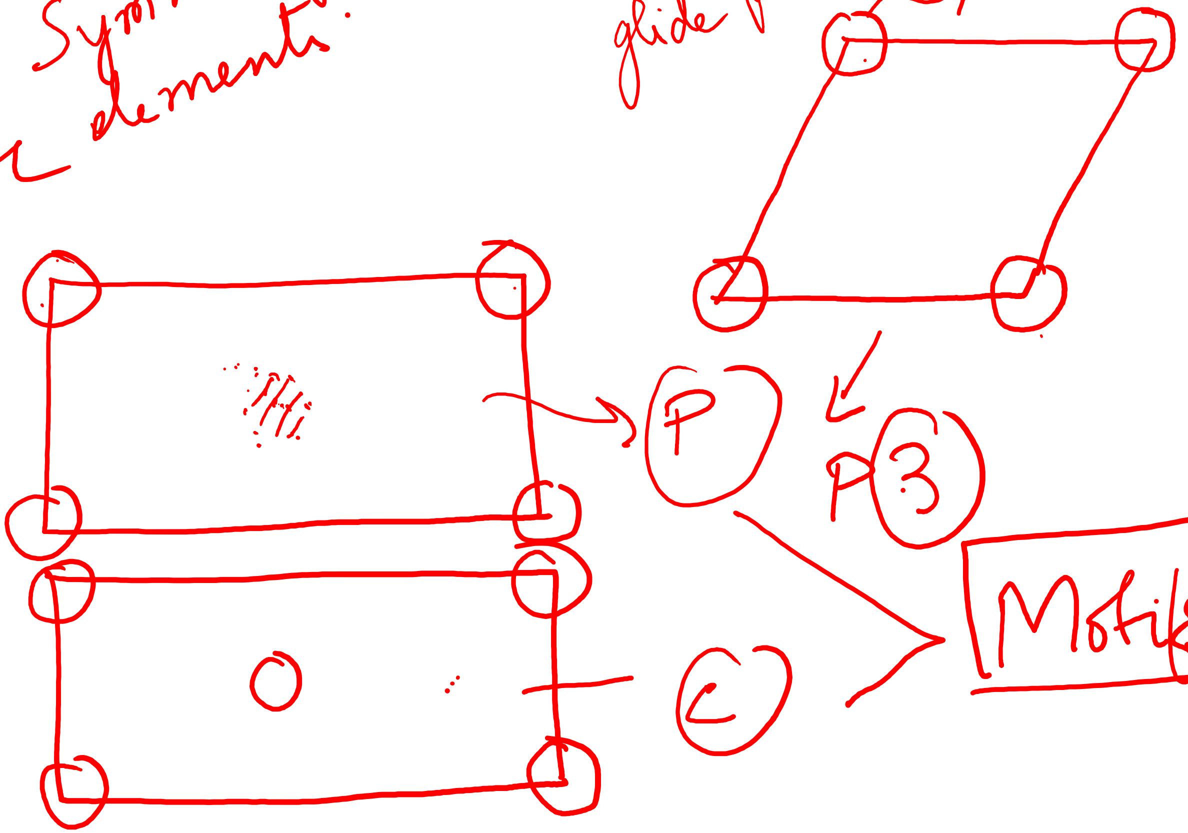


Symmetry elements

glide planes

Motifs/atoms





P

P3

C

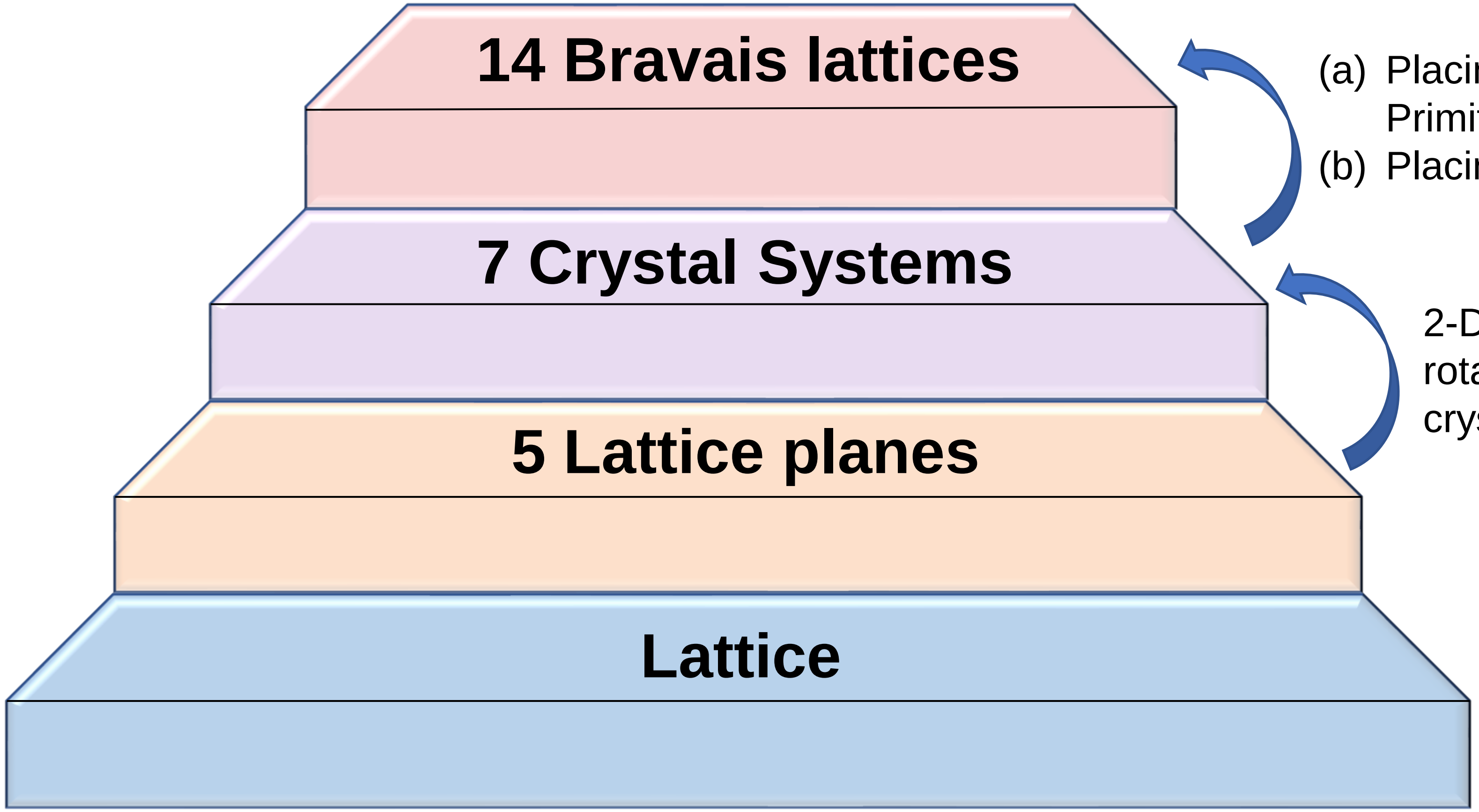
Motifs

Crystal Hierarchy

- Unique ways to arrange the lattice points in:

  2-D : 5

  3-D: 14



(a) Placing a lattice point in the centre of Primitive unit cells, or
(b) Placing lattice points in the middle of faces.

2-D lattices+ Constraint imposed by rotational symmetry upon the lattices = 7 crystal systems

MLL 100

Introduction to Materials Science and Engineering

Lecture-4

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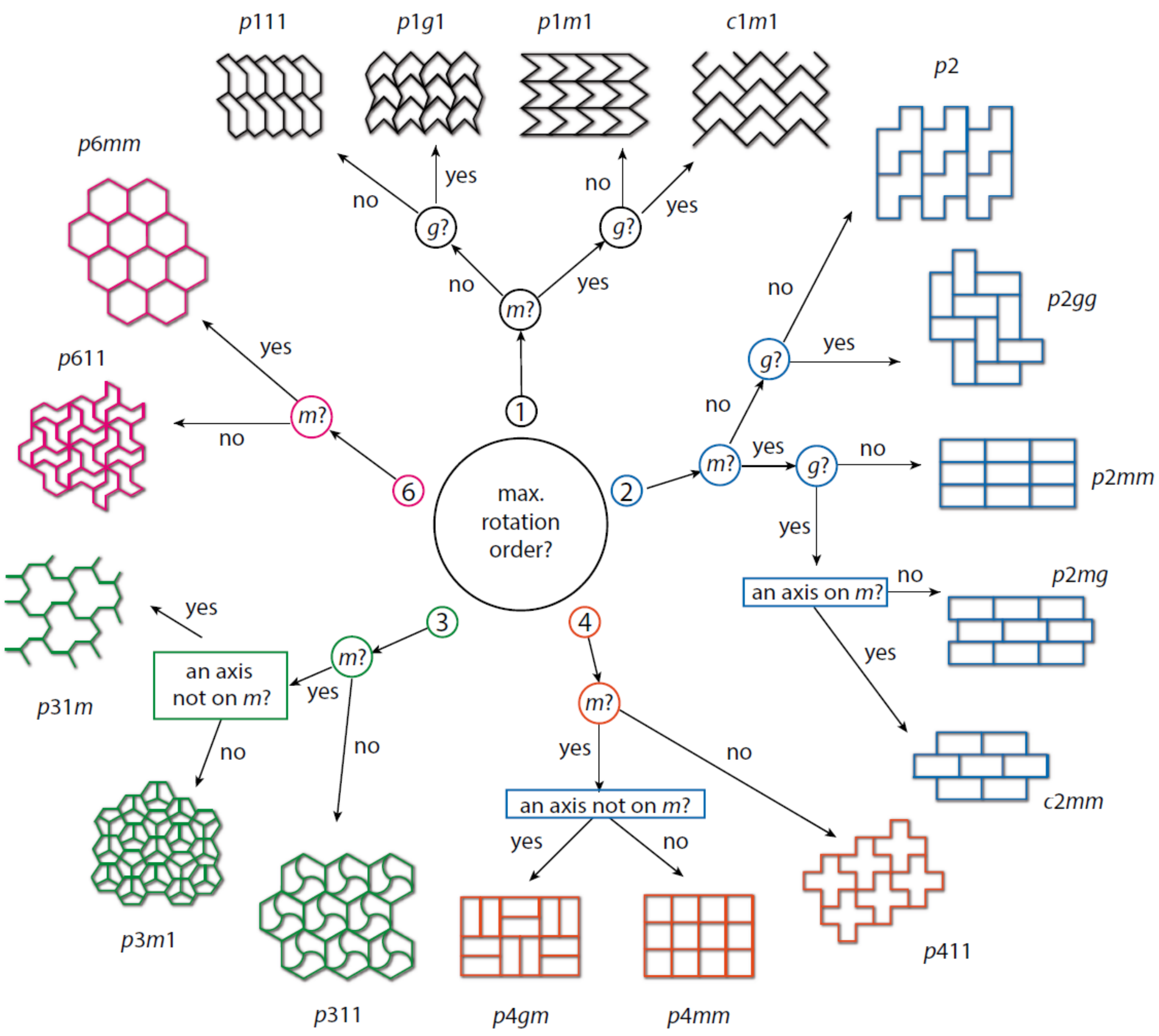
Department of Materials Science and Engineering

January 11, 2022

What we learnt in Lecture-3?

- Primitive and non-primitive unit cell
- Lattice point calculation per unit cell (2-D)
- 2-D lattices
- Plane groups

Algorithm for plane group determination



1) What is the rotation axis of highest order?

2) Is mirror plane present?

3) Is glide plane (g) present which does not result from any combination of rotation, translation and reflection?

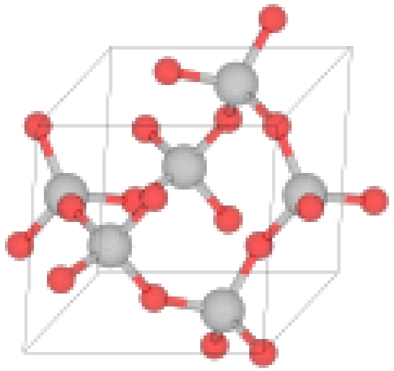
4) Is any rotation axis of arbitrary order (not necessarily the one with the highest
5) order) present but not on a mirror?

6) Is rotation axis of any order present on a mirror?

Crystal

Homogeneous, anisotropic solid states, whose building blocks are three-dimensional periodically ordered

krystallos



Quartz

Homogeneous: Uniform chemical composition

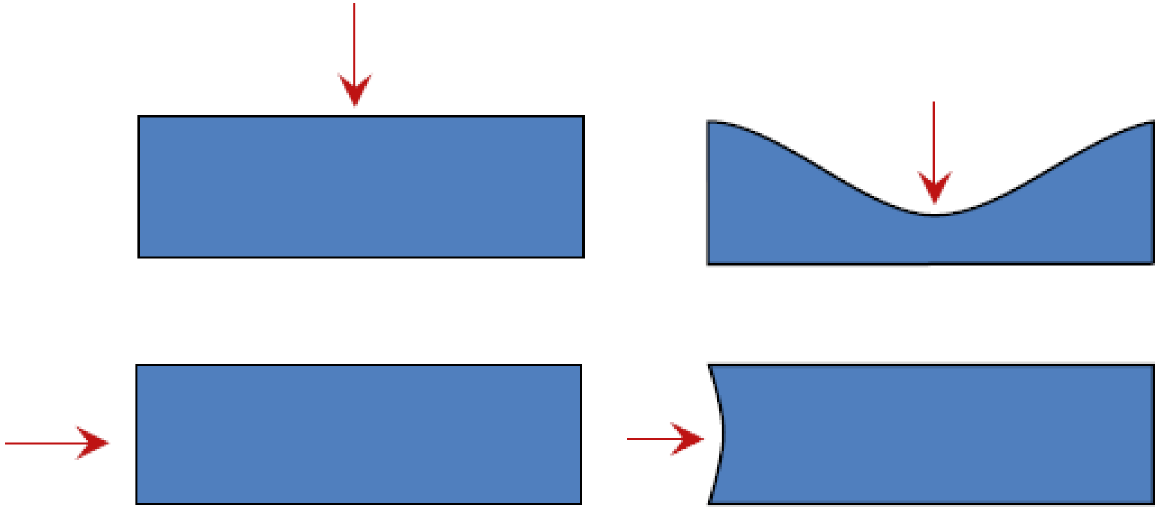
Milk

Horlicks

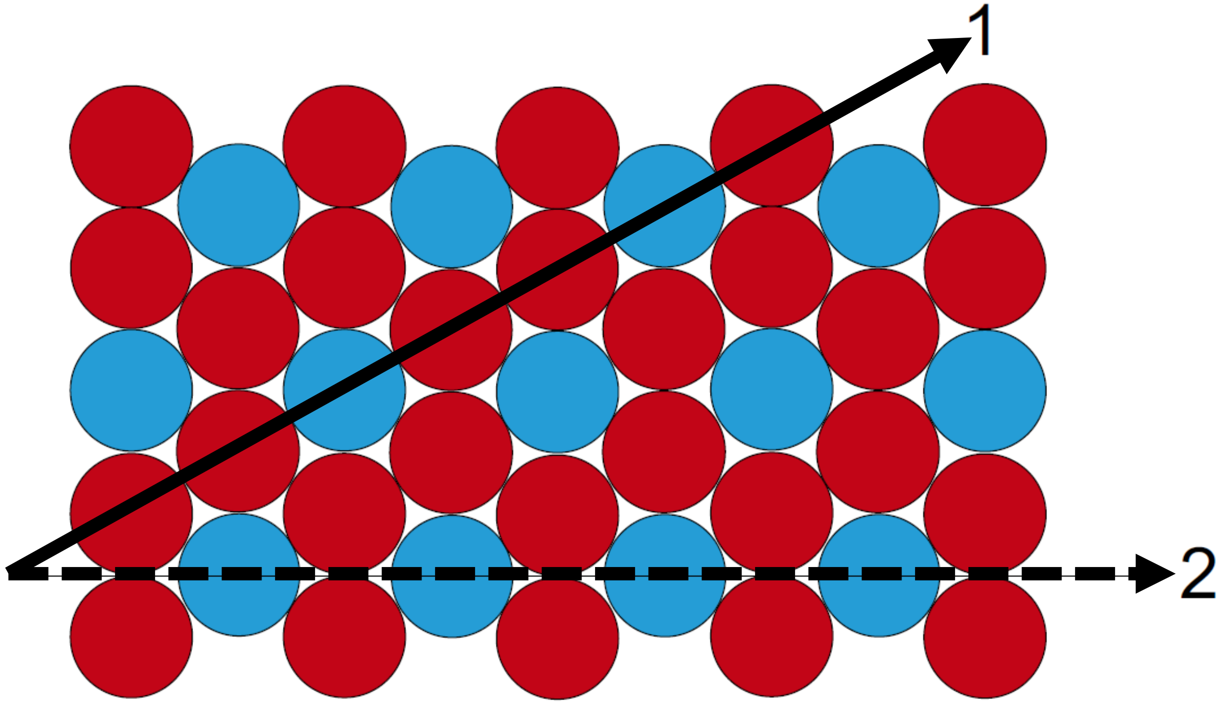
Milk with honey

Anisotropy

- Directional dependent properties



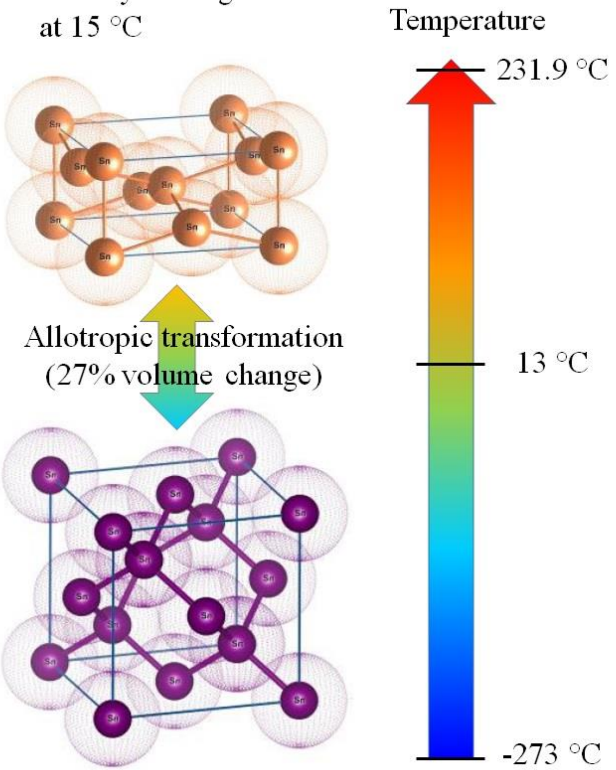
Application of pressure along different directions



Importance of crystal systems

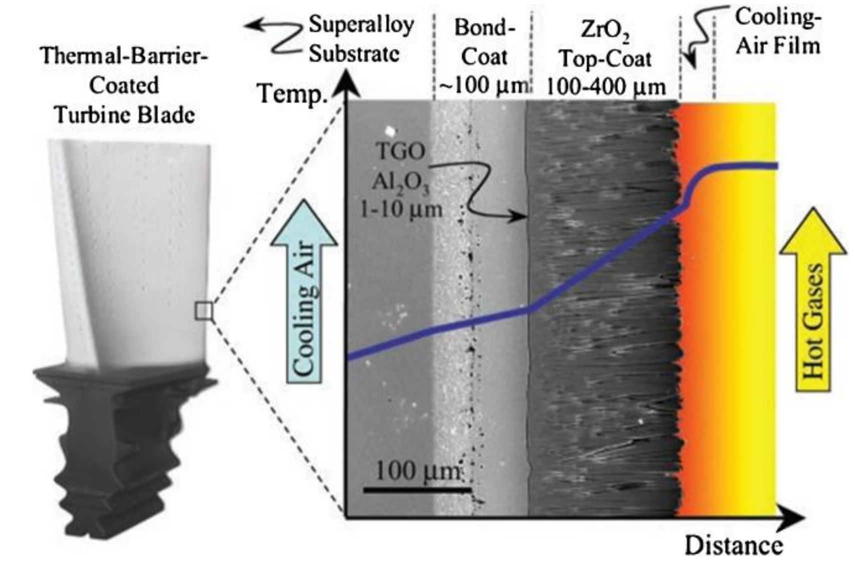
Color: White
β-tin
(Body Centered Tetragonal)
a = 5.831 Å, c = 3.181 Å

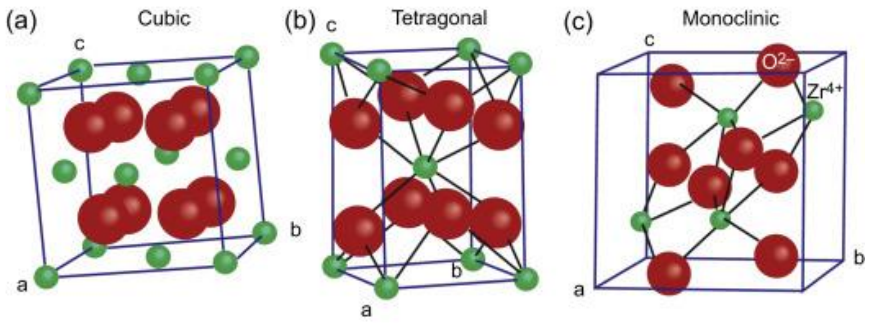
Density: 7.29 g/cm^3
at 15 °C

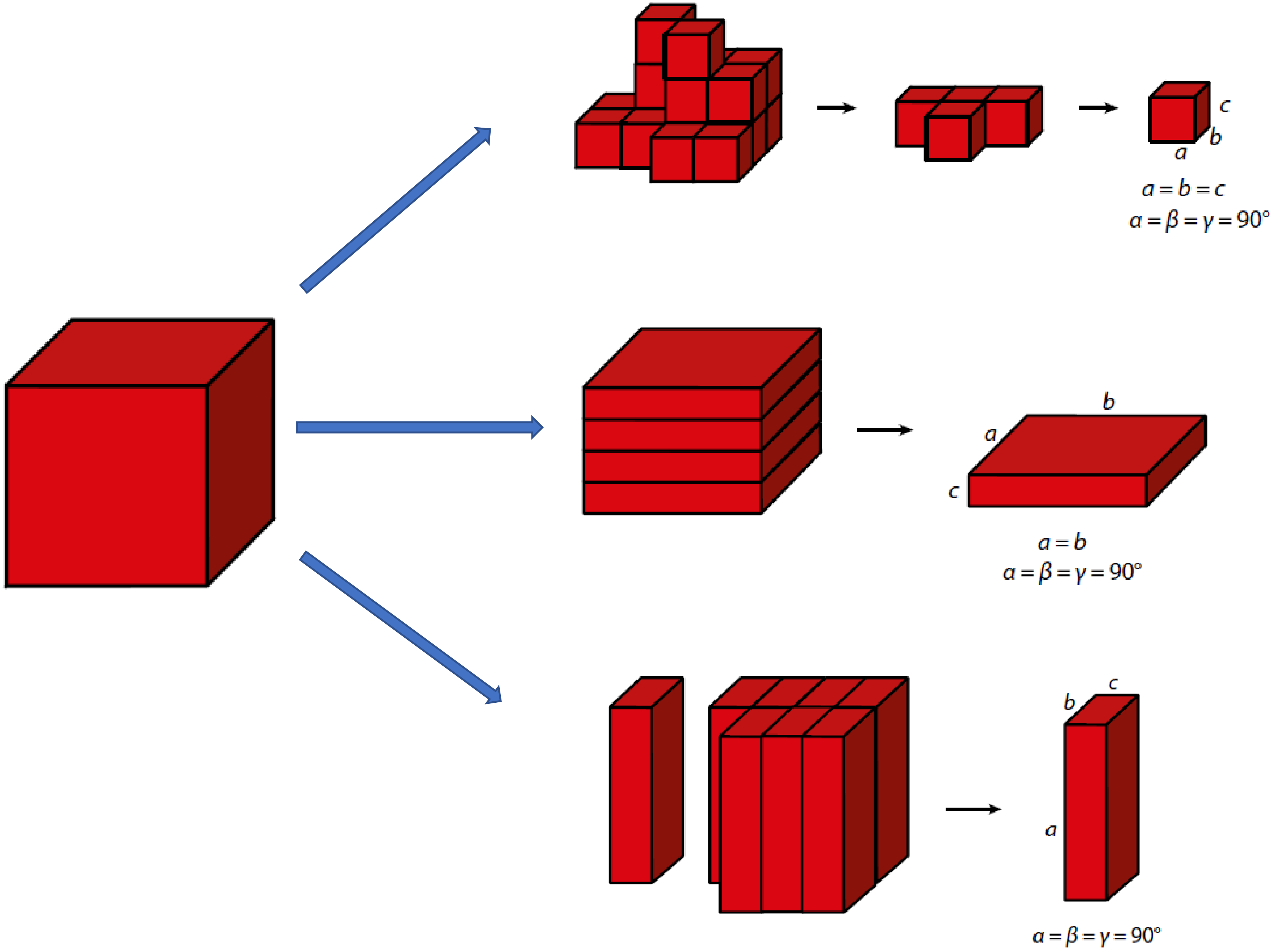


Color: Grey
α-tin (Diamond cube)
a = 6.489 Å

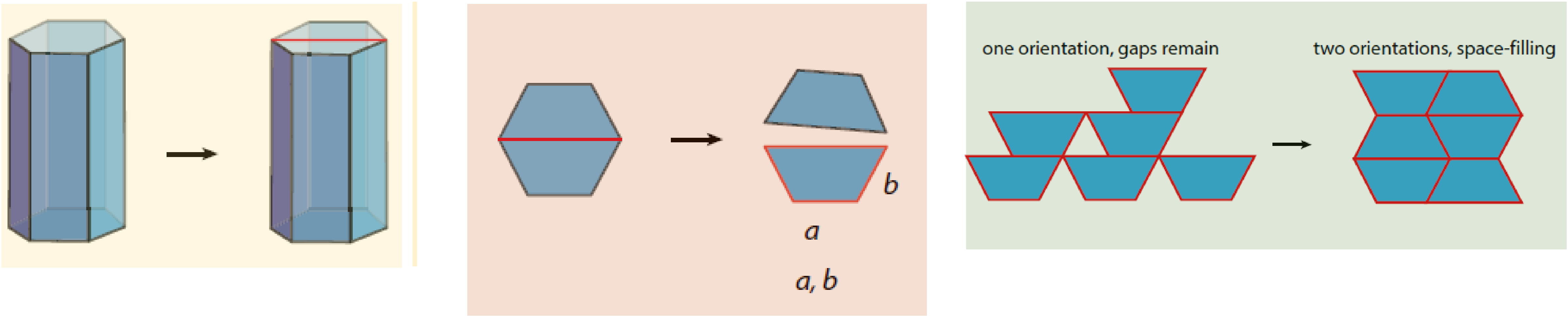
Density: 5.77 g/cm^3
at 13 °C



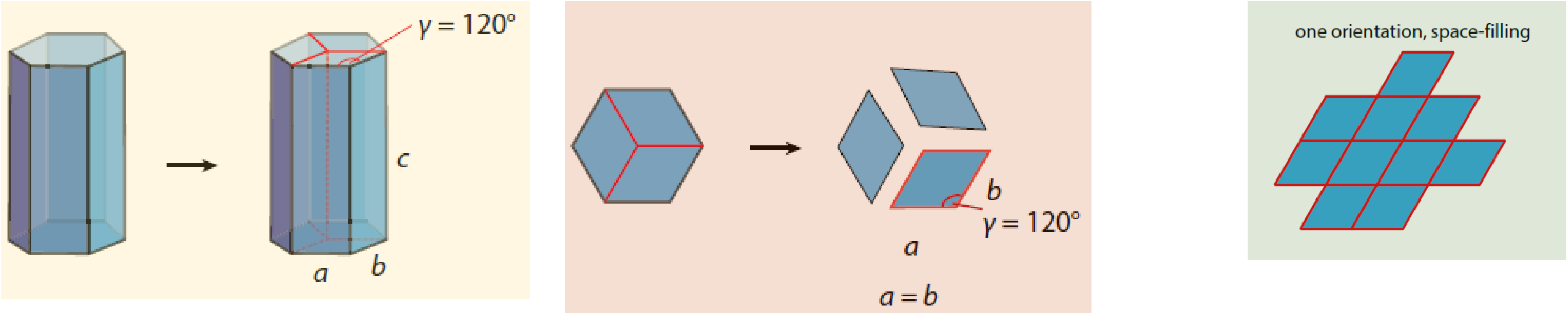




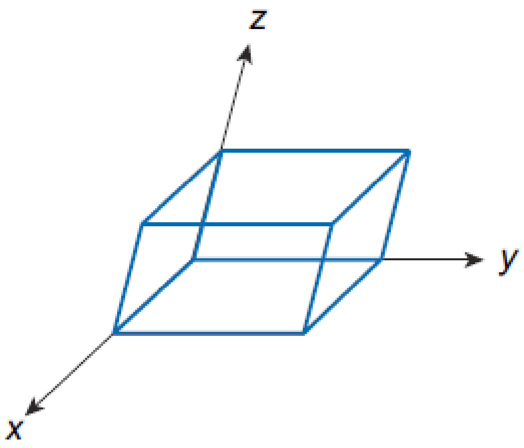
c
b
a
$a = b = c$
$\alpha = \beta = \gamma = 90°$
b
a
c
$a = b$
$\alpha = \beta = \gamma = 90°$
c
b
a
$\alpha = \beta = \gamma = 90°$

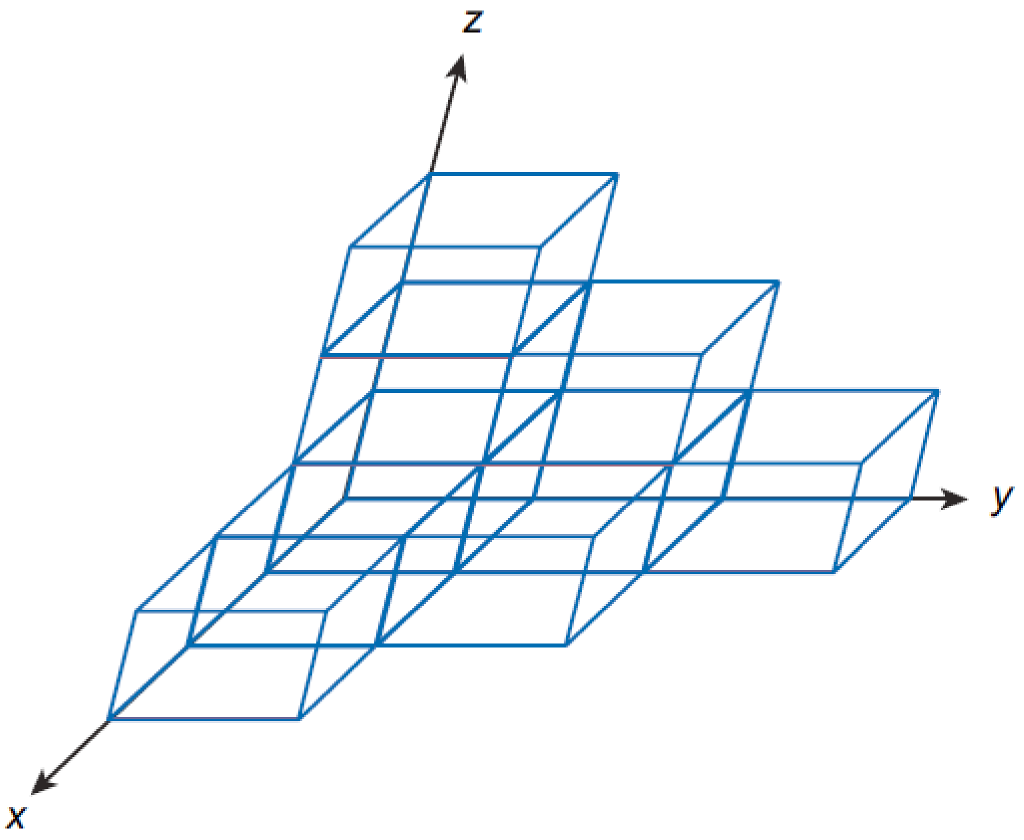


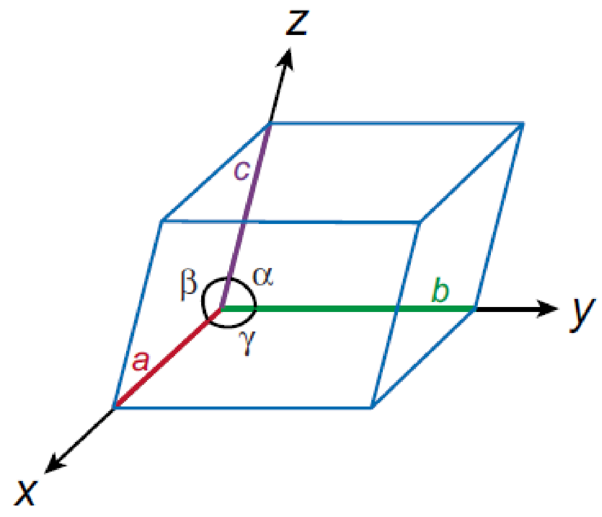
b
a
a, b
one orientation, gaps remain
two orientations, space-filling



$\gamma = 120°$
c
a
b
b
$\gamma = 120°$
a
$a = b$
one orientation, space-filling





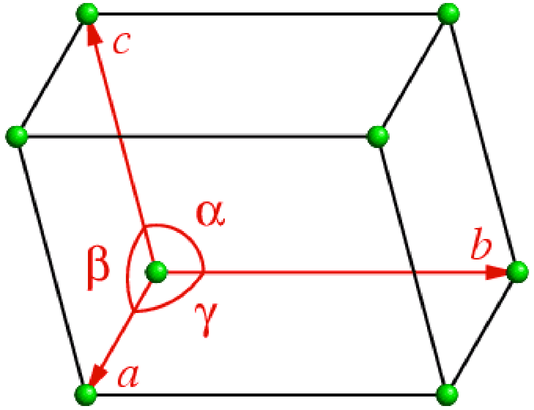


Unit cell: Smallest unit which builds up the entire crystal by repeating translations along all three spatial directions

Crystal systems

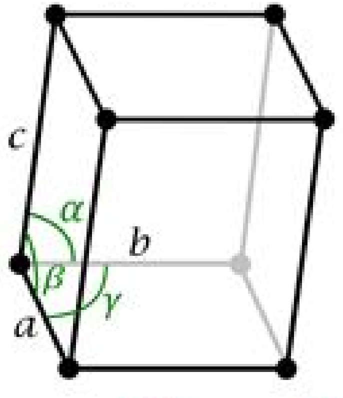
1 Triclinic

$a \neq b \neq c;\ \alpha \neq \beta \neq \gamma$



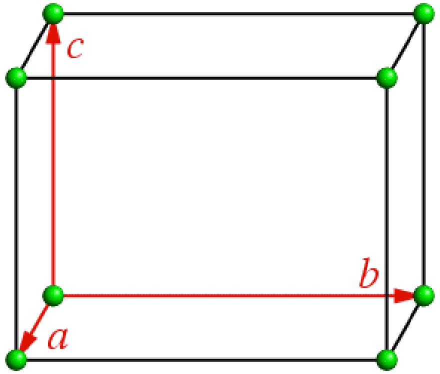
2 Monoclinic

$a \neq b \neq c;\ \alpha = \gamma = 90° \neq \beta$



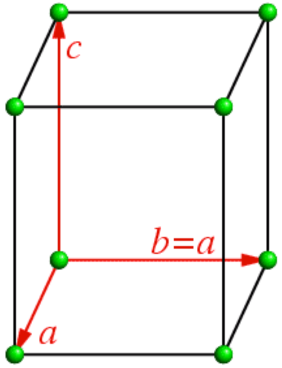
3 Orthorhombic

$a \neq b \neq c;\ \alpha = \beta = \gamma = 90°$



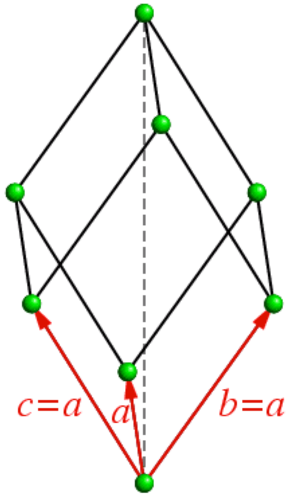
4 Tetragonal

$a = b \neq c;\ \alpha = \beta = \gamma = 90°$



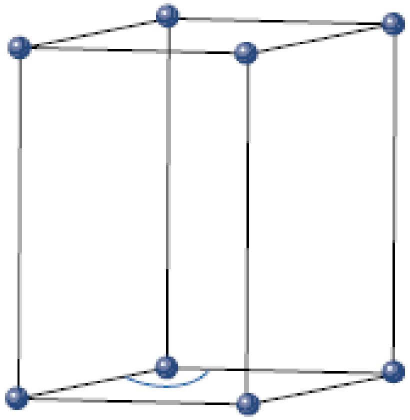
5 Trigonal

$a = b = c;\ \alpha = \beta = \gamma \neq 90°$



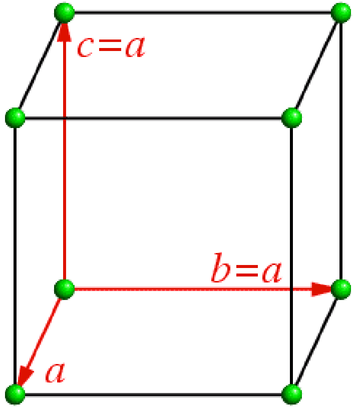
6 Hexagonal

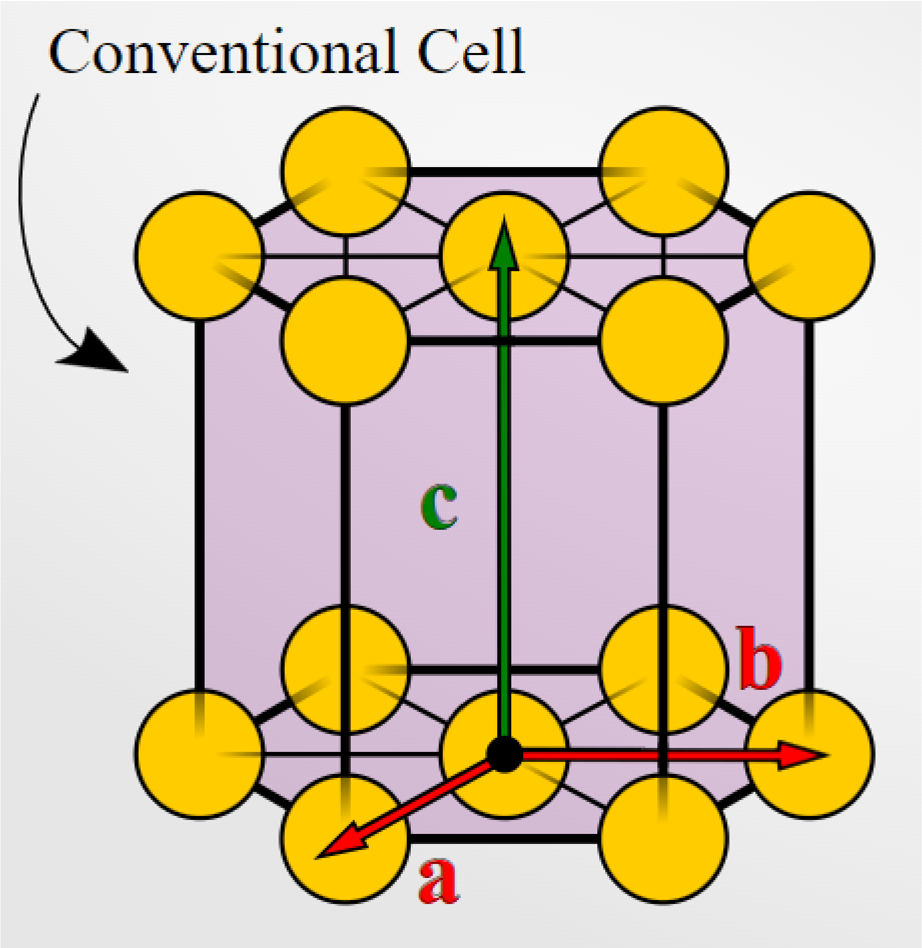
$a = b \neq c;\ \alpha = \beta = 90°;\ \gamma = 120°$

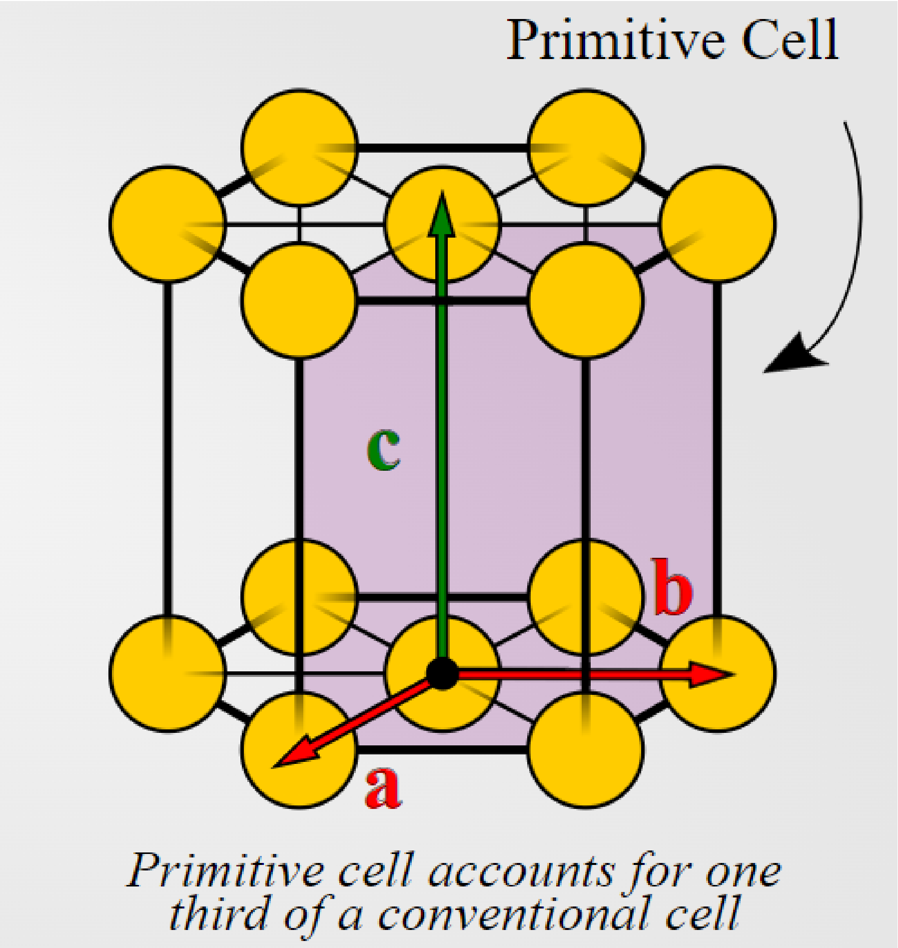


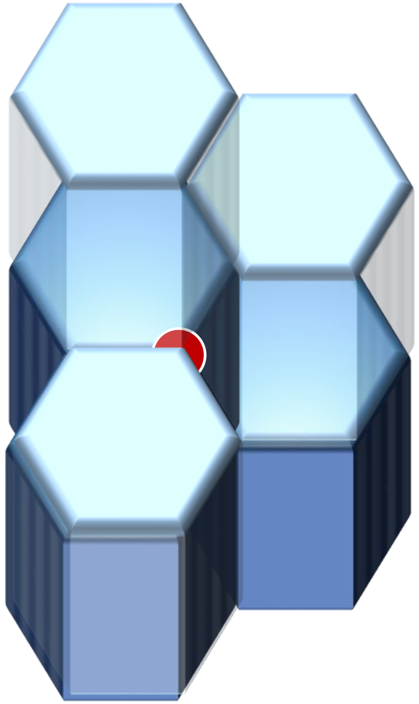
7 Cubic

$a = b = c;\ \alpha = \beta = \gamma = 90°$



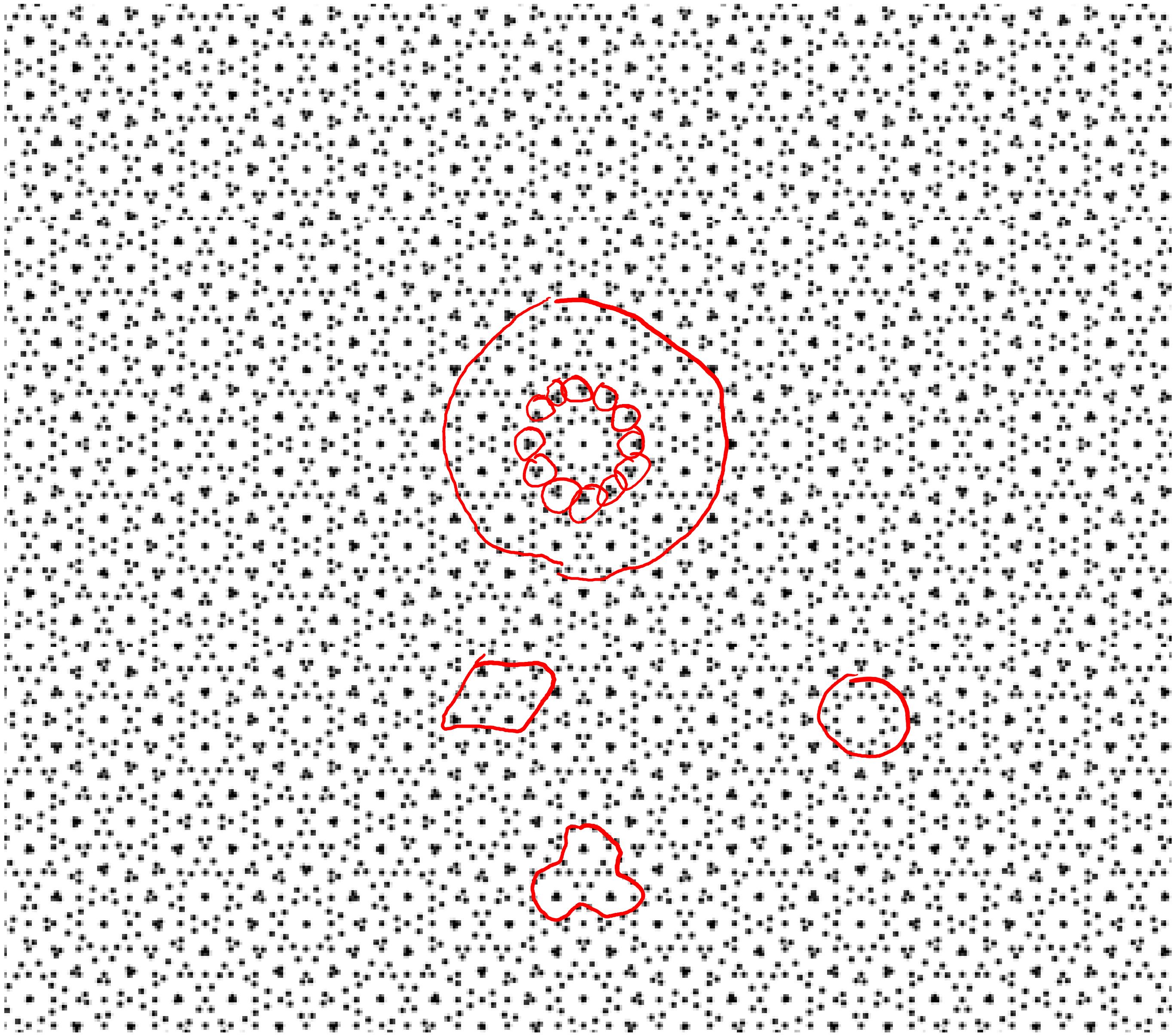




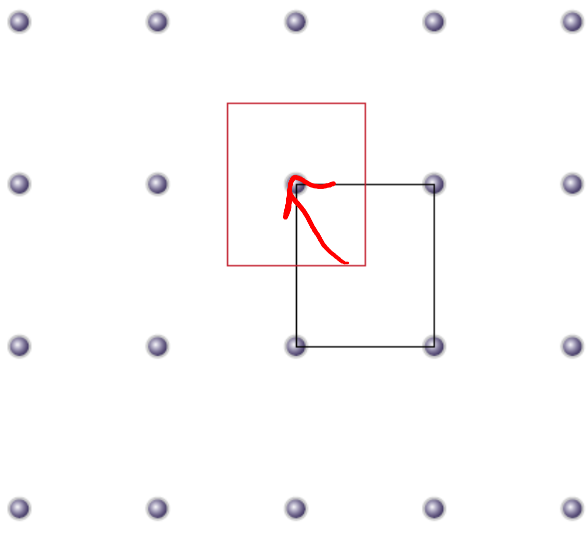


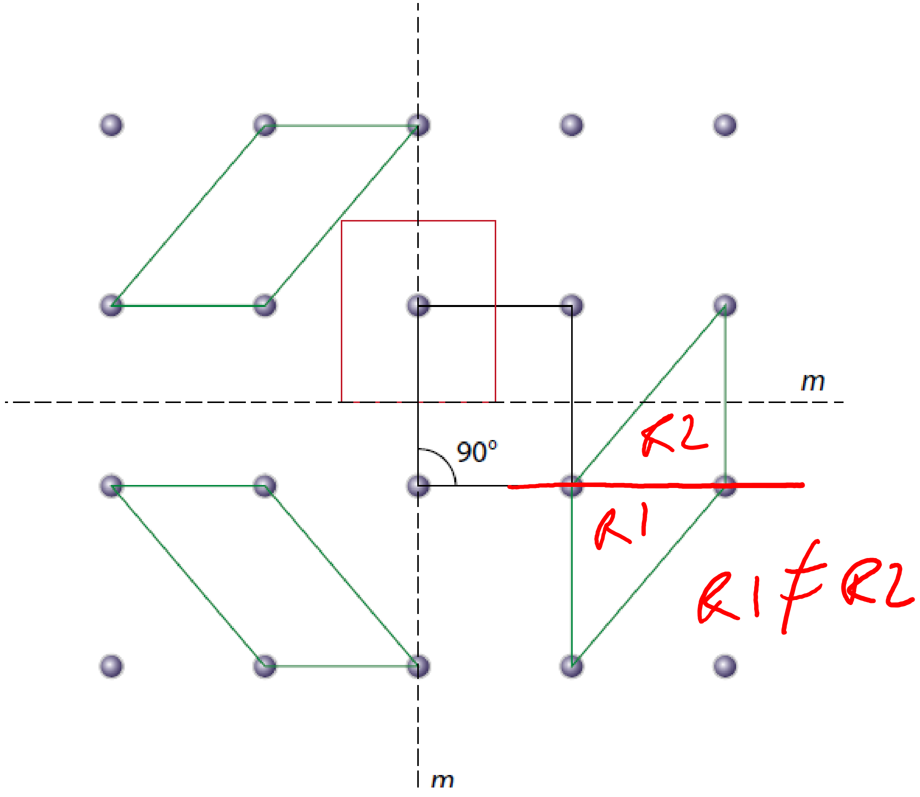
How many atoms per unit cell in a conventional cell?

Three

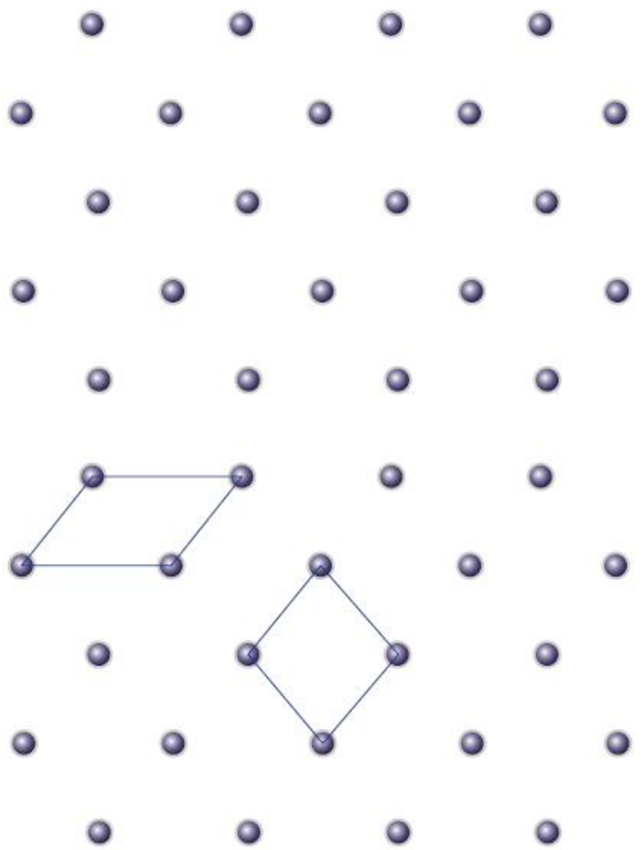


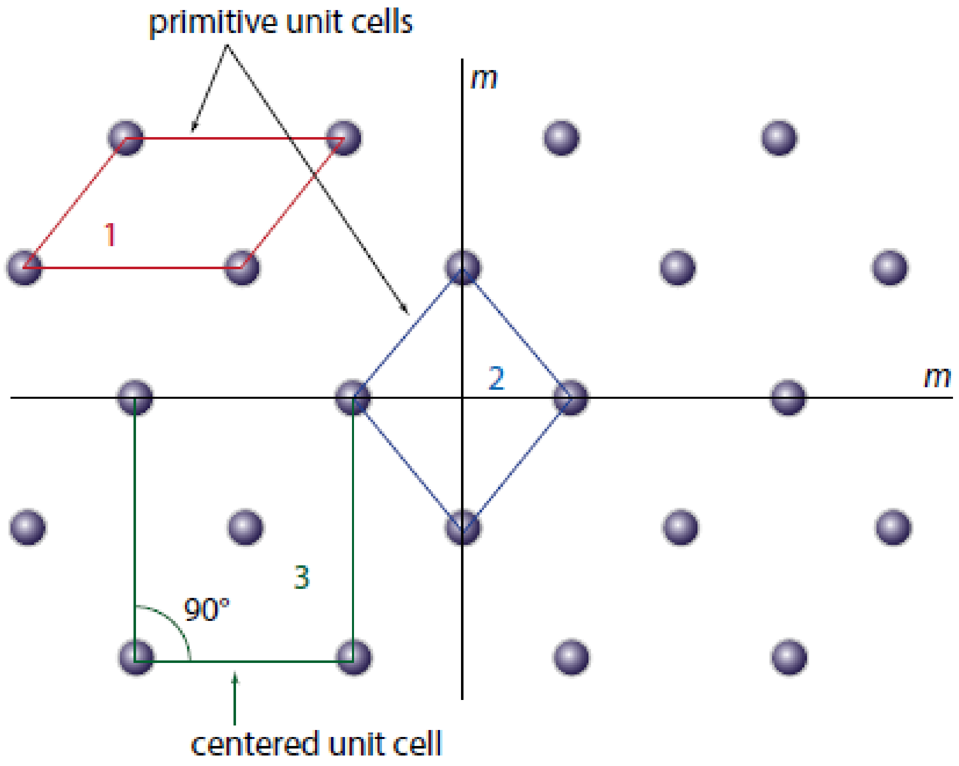
Marroquin pattern

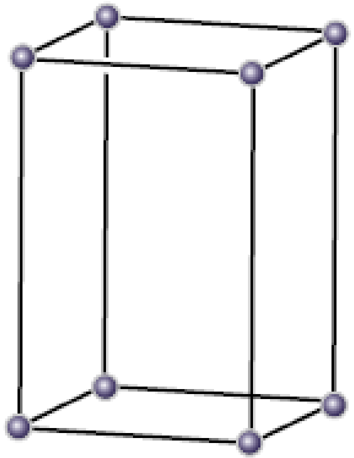




- Unit cell as small as possible -----> Lattice vectors as short as possible.
- Unit cell should reflect the symmetry of the lattice -----> Lattice vectors should run parallel to symmetry axes or perpendicular to planes of symmetry.
- Lattice vectors should be orthogonal (or hexagonal) -----> Enclose an angle of 90° (or 120°)

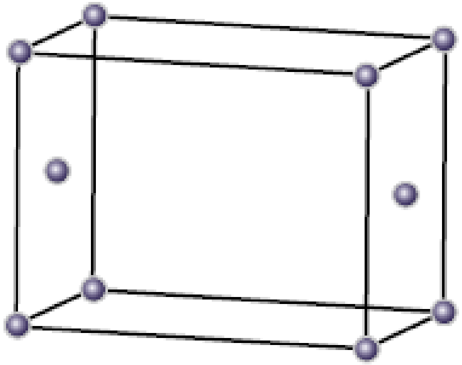



primitive unit cells
m
1
2
m
3
90°
centered unit cell



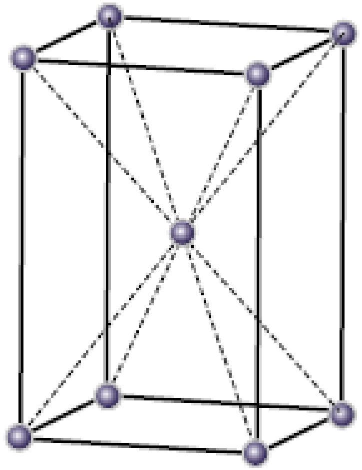
primitive

P



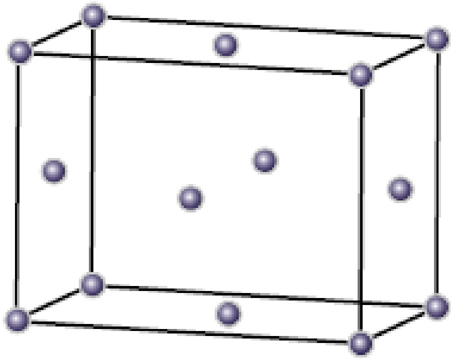
single-sided face-centered

C(AB)



body-centered

I

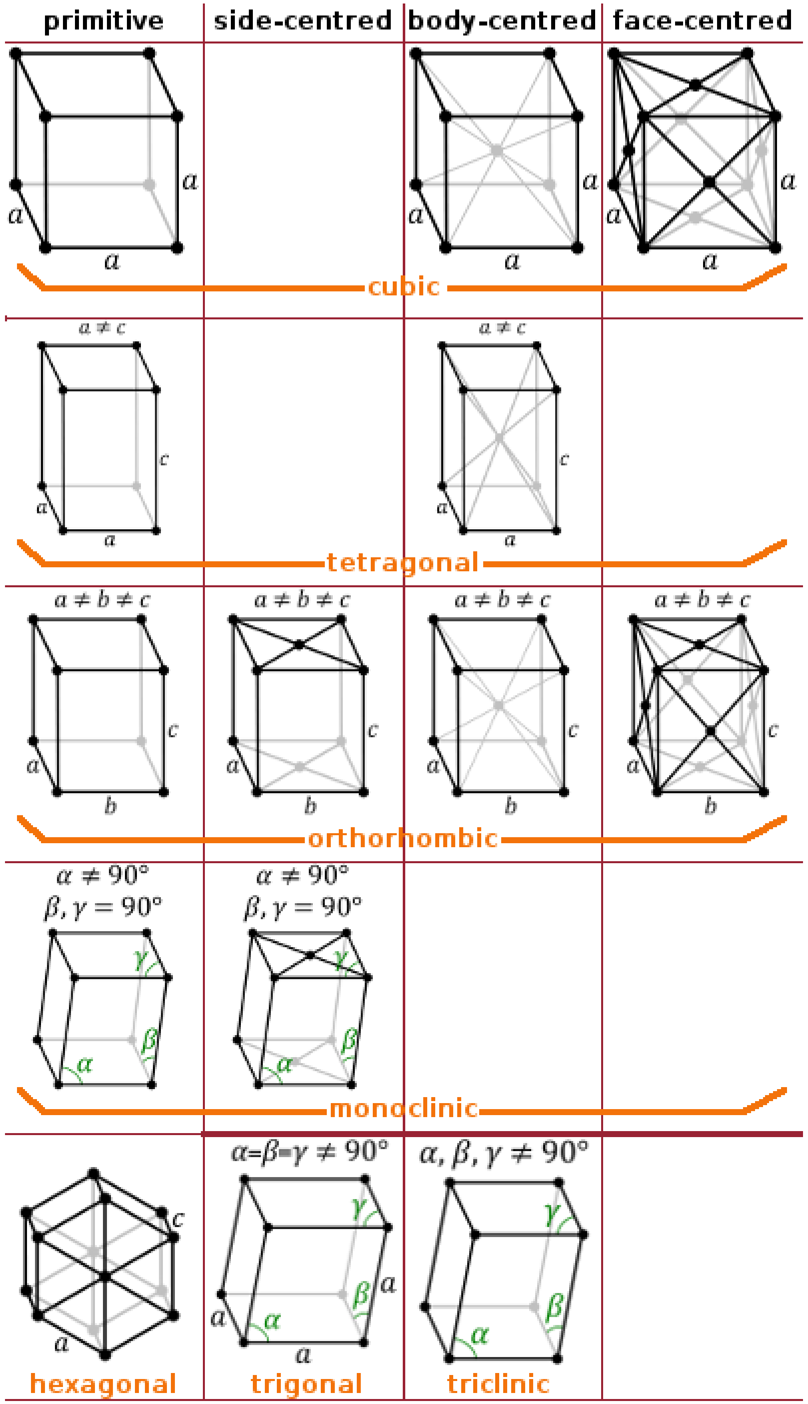


all-sided face-centered

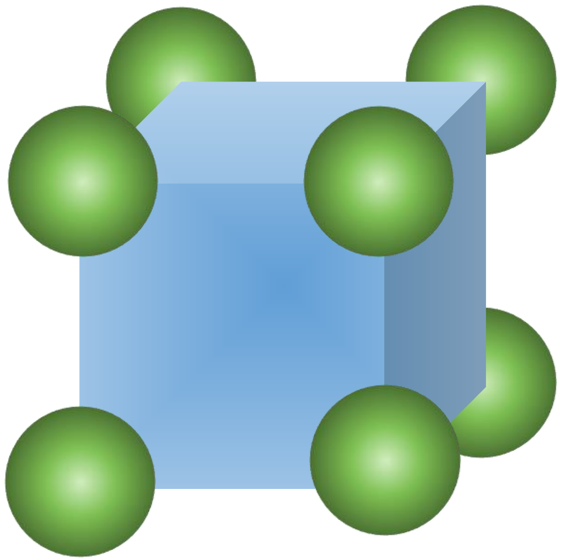
F

End- centred

14 Bravais lattices

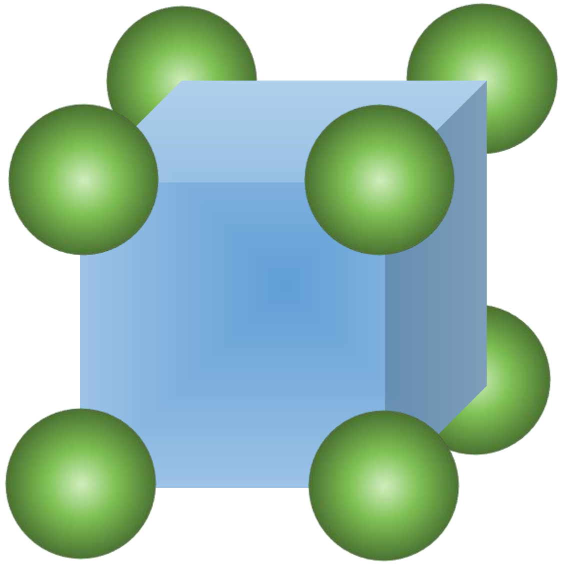


Simple Cubic (**P**)



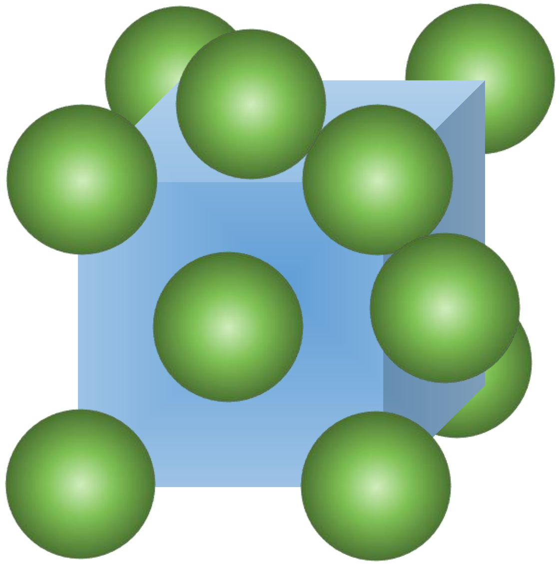
(Atoms located only at the corners of the unit cell)

Body centred Cubic (**I**)



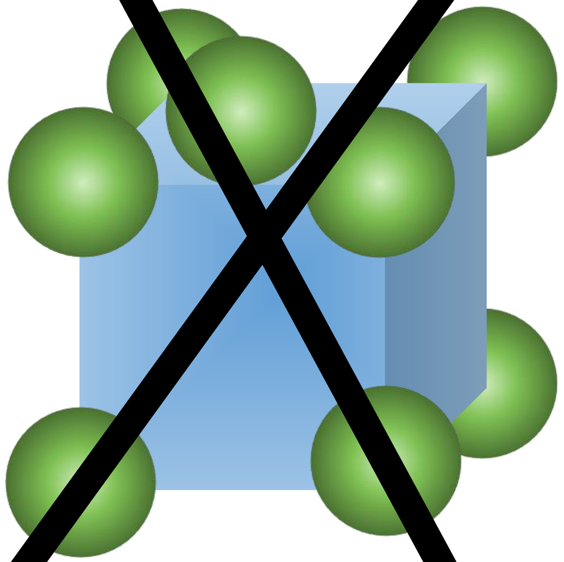
(Atoms located at the corners and centre of the unit cell)

Face centred Cubic (**F**)

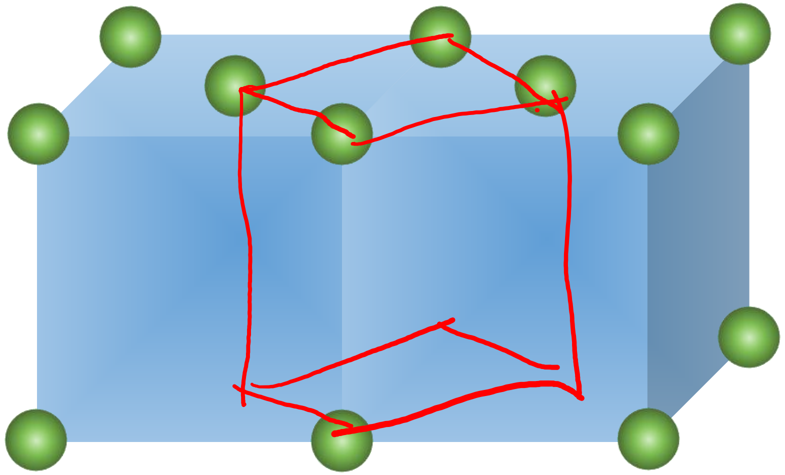


(Atoms located at the corners and faces of the unit cell)

~~End centred Cubic~~



~~*(Atoms located at the corners and one of the opposite faces of the unit cell)*~~



Why is there no end-centred cubic unit cell?

End-centred cubic ~ Primitive Tetragonal

- Why is there no body-centred monoclinic Bravais lattice?

- Why can not a face centred cubic lattice be considered a body-centred tetragonal lattice?

MLL 100

Introduction to Materials Science and Engineering

Lecture-5

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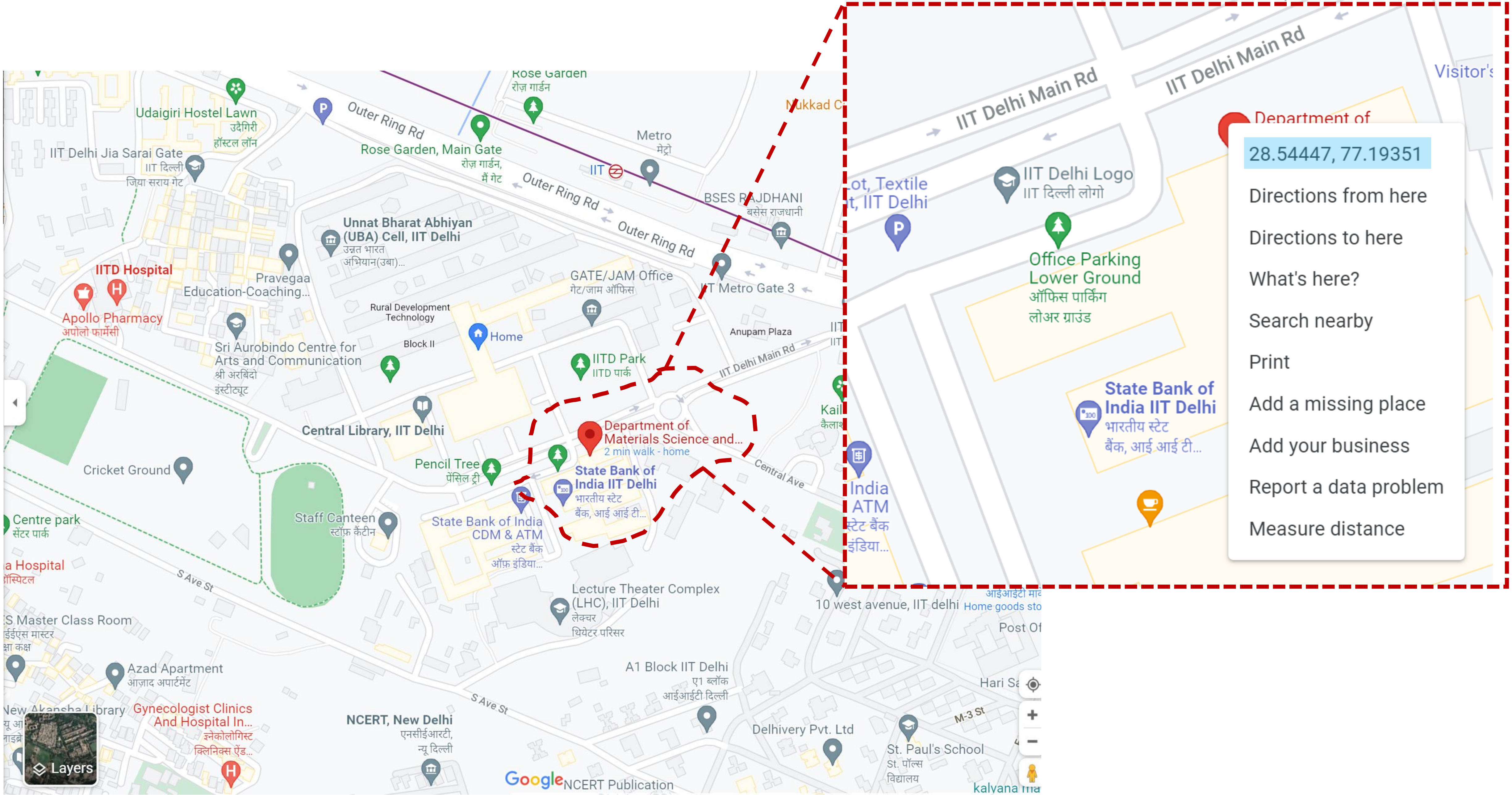
IIT Delhi
Department of Materials Science and Engineering

January 12, 2022

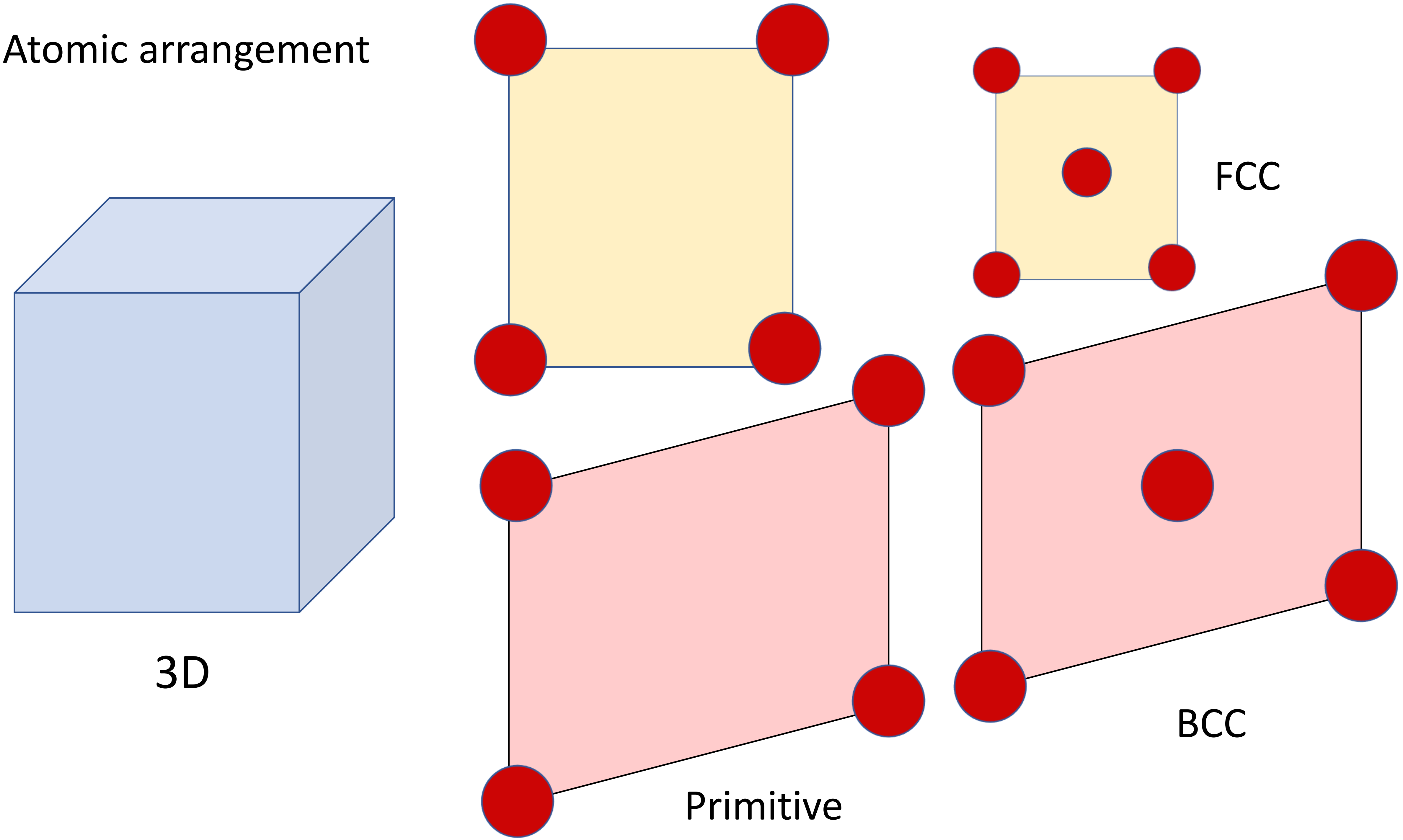
What we learnt in Lecture-4?

- Crystal
- Crystal systems
- Bravais lattices

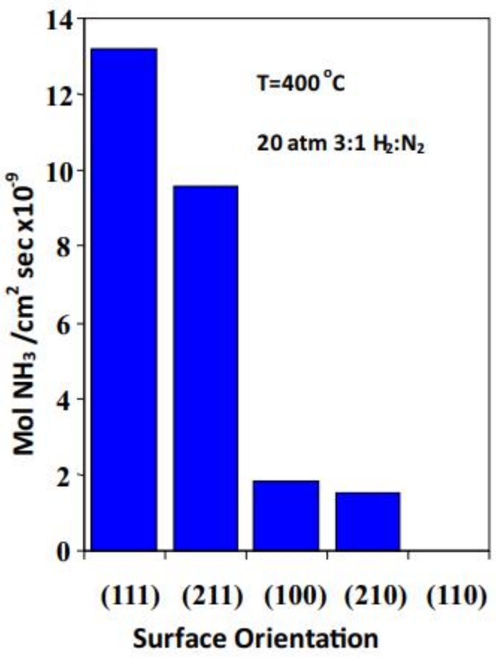


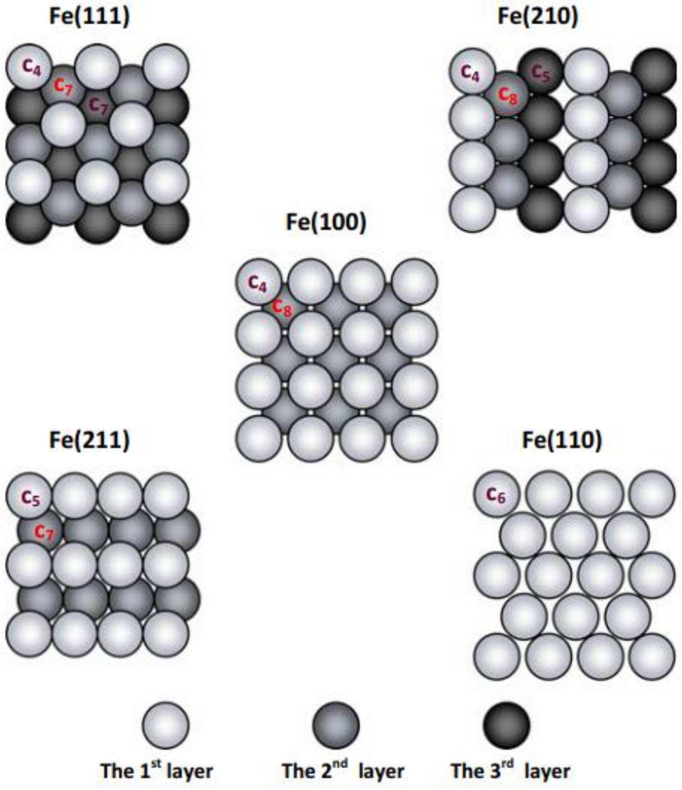
Udaigiri Hostel Lawn
IIT Delhi Jia Sarai Gate
Outer Ring Rd
Rose Garden
Rose Garden, Main Gate
Metro
IIT
BSES RAJDHANI
Unnat Bharat Abhiyan (UBA) Cell, IIT Delhi
IITD Hospital
Pravegaa Education-Coaching...
Apollo Pharmacy
GATE/JAM Office
IIT Metro Gate 3
Rural Development Technology
Block II
Home
Anupam Plaza
Sri Aurobindo Centre for Arts and Communication
IITD Park
IIT Delhi Main Rd
Central Library, IIT Delhi
Department of Materials Science and...
2 min walk - home
Cricket Ground
Pencil Tree
State Bank of India IIT Delhi
Central Ave
Centre park
Staff Canteen
State Bank of India CDM & ATM
a Hospital
S Ave St
Lecture Theater Complex (LHC), IIT Delhi
10 west avenue, IIT delhi
Home goods sto
Post Of
S Master Class Room
Azad Apartment
A1 Block IIT Delhi
Hari Sa
New Akansha Library
Gynecologist Clinics And Hospital In...
NCERT, New Delhi
Delhivery Pvt. Ltd
M-3 St
St. Paul's School
Layers
Google
NCERT Publication
kalyana
IIT Delhi Main Rd
Visitor's
Department of
IIT Delhi Logo
ot, Textile
t, IIT Delhi
Office Parking Lower Ground
State Bank of India IIT Delhi
India ATM
28.54447, 77.19351
Directions from here
Directions to here
What's here?
Search nearby
Print
Add a missing place
Add your business
Report a data problem
Measure distance

Atomic arrangement

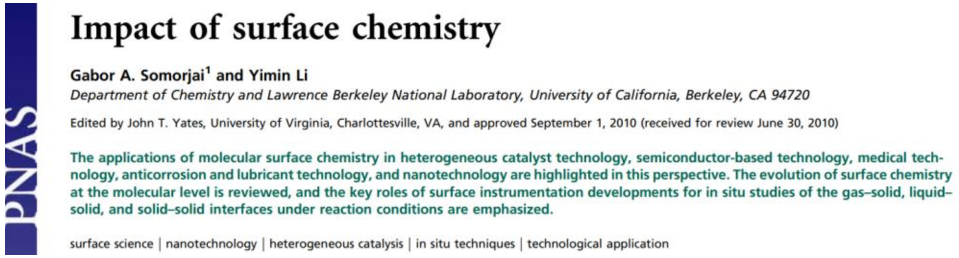


Reactivity of crystalline surfaces





(111) and (211) faces are the most reactive surfaces.


PNAS

Impact of surface chemistry

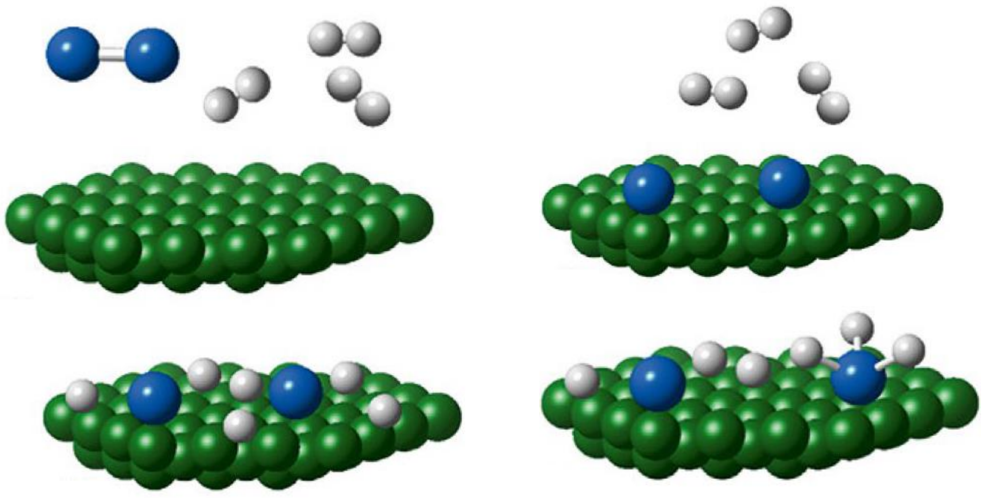
Gabor A. Somorjai[1] and Yimin Li

Department of Chemistry and Lawrence Berkeley National Laboratory, University of California, Berkeley, CA 94720

Edited by John T. Yates, University of Virginia, Charlottesville, VA, and approved September 1, 2010 (received for review June 30, 2010)

The applications of molecular surface chemistry in heterogeneous catalyst technology, semiconductor-based technology, medical technology, anticorrosion and lubricant technology, and nanotechnology are highlighted in this perspective. The evolution of surface chemistry at the molecular level is reviewed, and the key roles of surface instrumentation developments for in situ studies of the gas–solid, liquid–solid, and solid–solid interfaces under reaction conditions are emphasized.

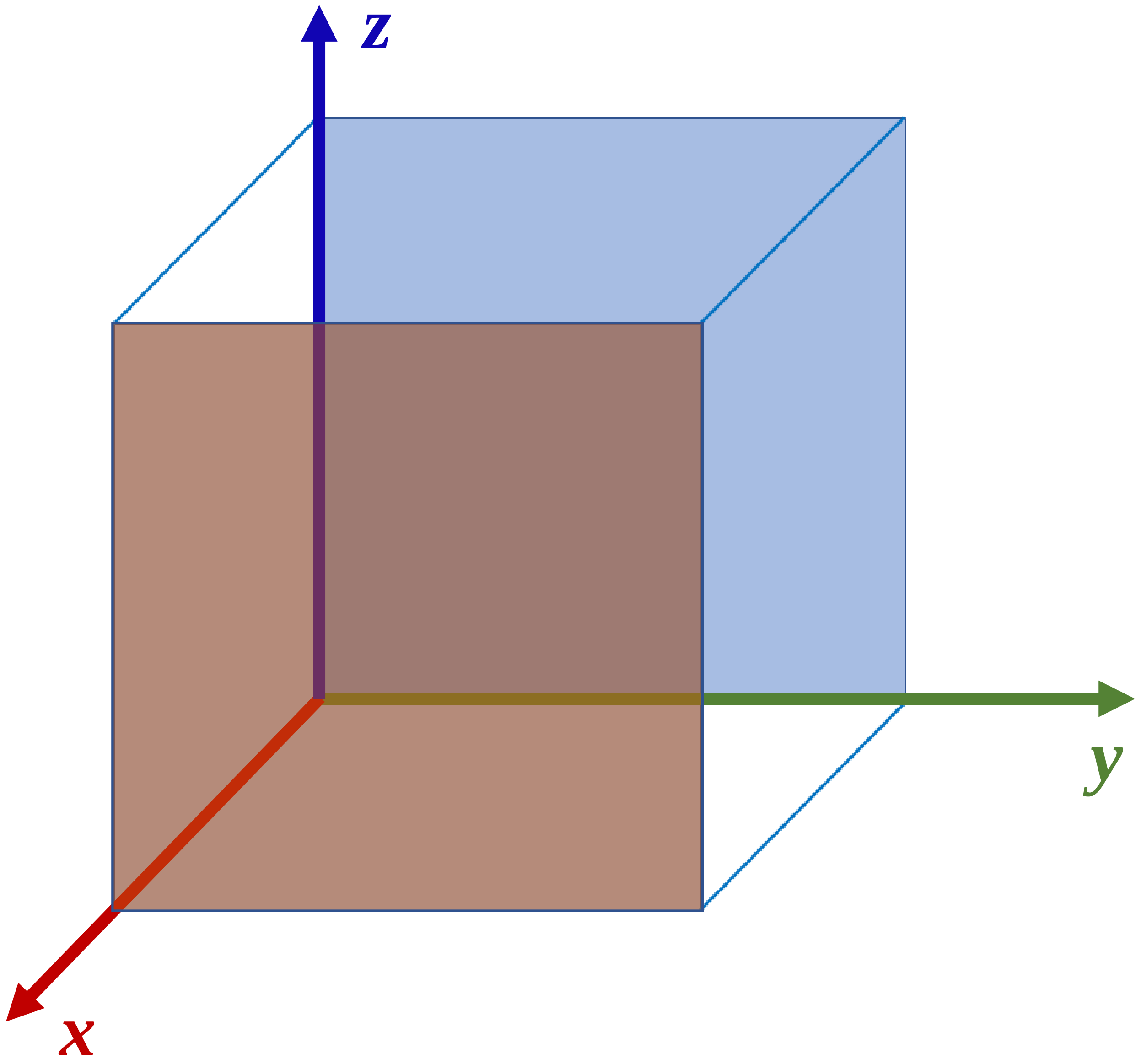
surface science | nanotechnology | heterogeneous catalysis | in situ techniques | technological application



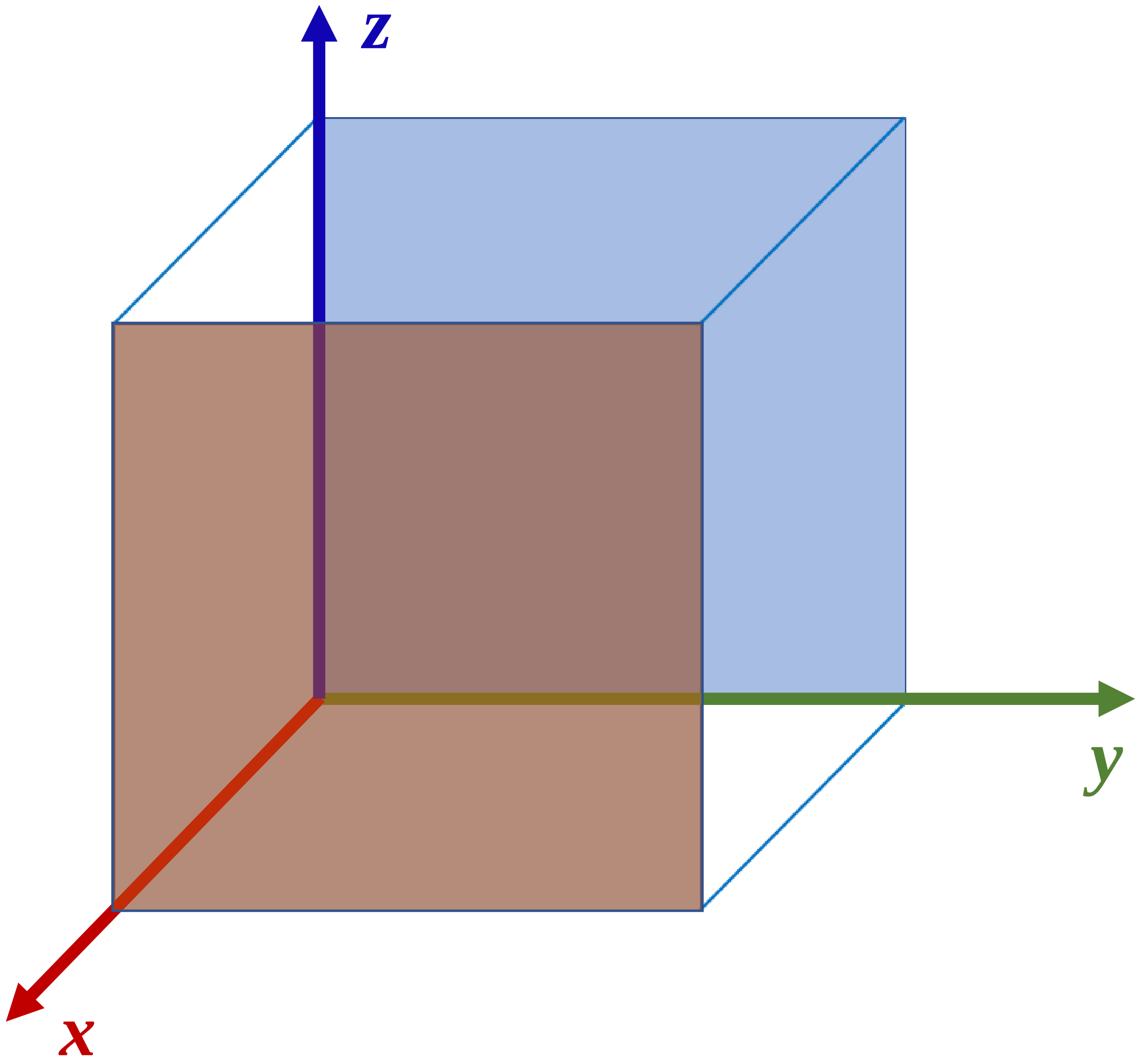
When do you tend to express your emotional reactivity?

Bonds decide the stability of a crystal --------> Understanding the bonds needs learning about the planes, directions and atomic arrangement

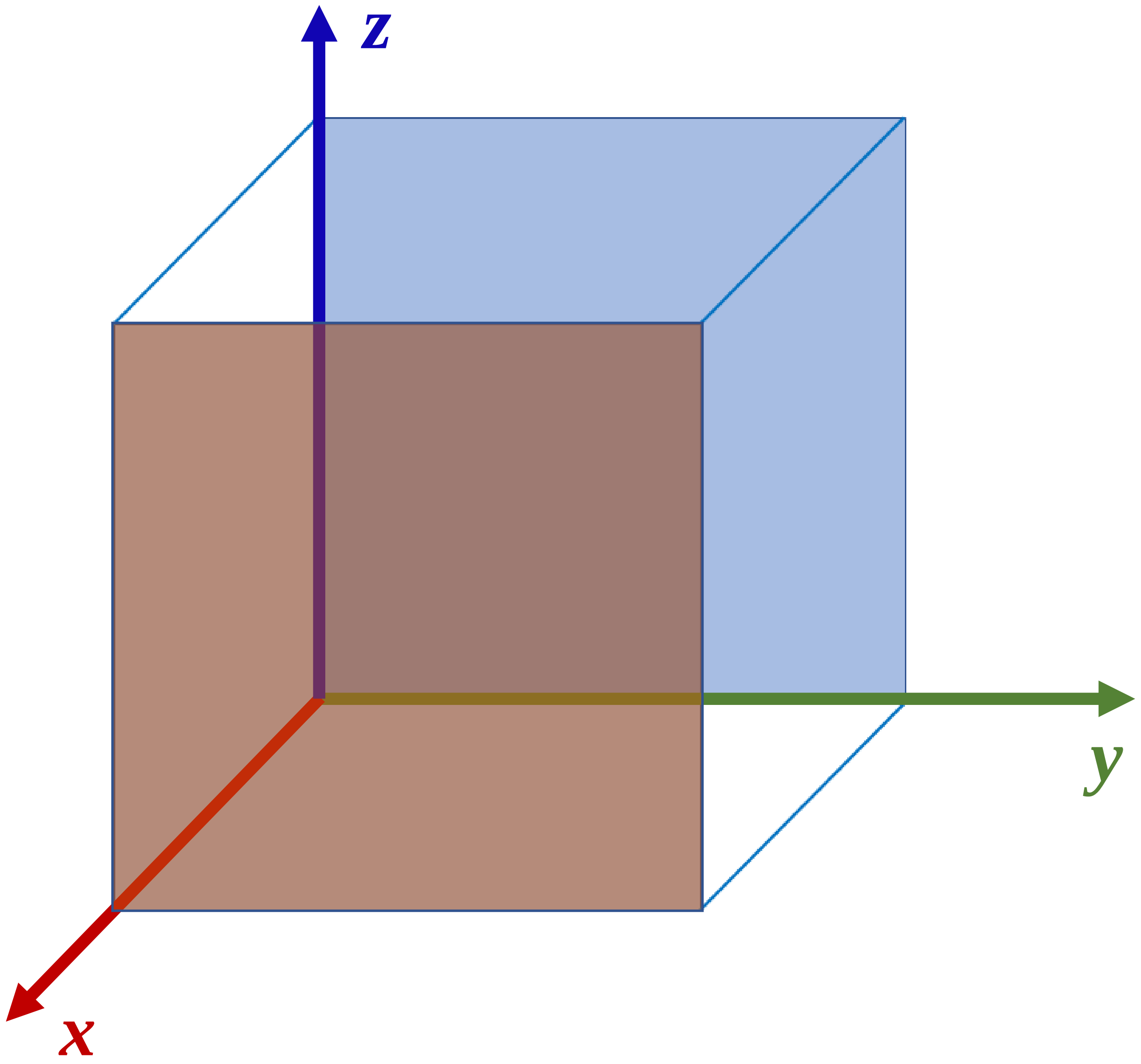
Miller indices ------ (Faces of a cube)



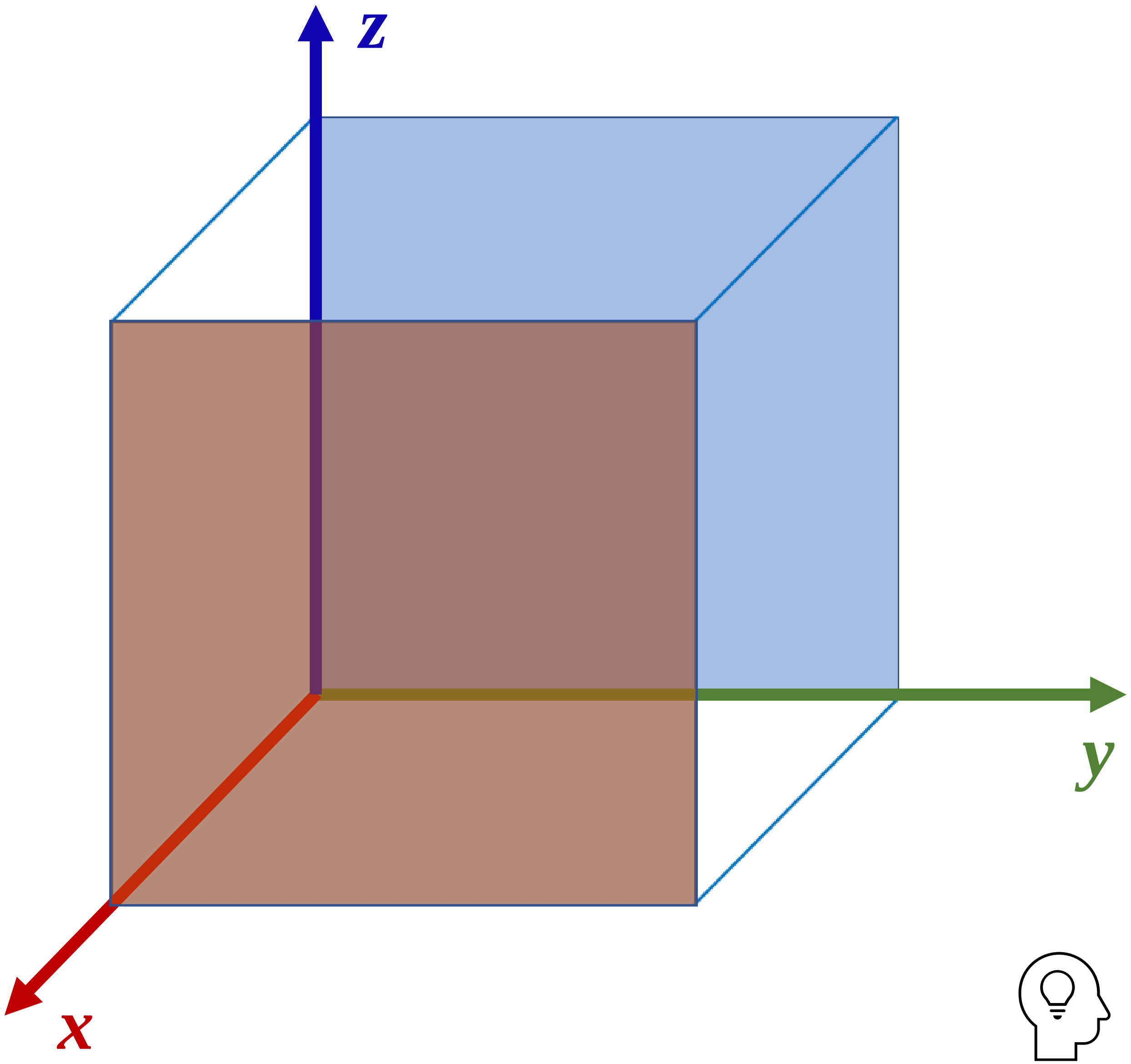
Miller indices ------ (Faces of a cube)



Miller indices ------ (Faces of a cube)

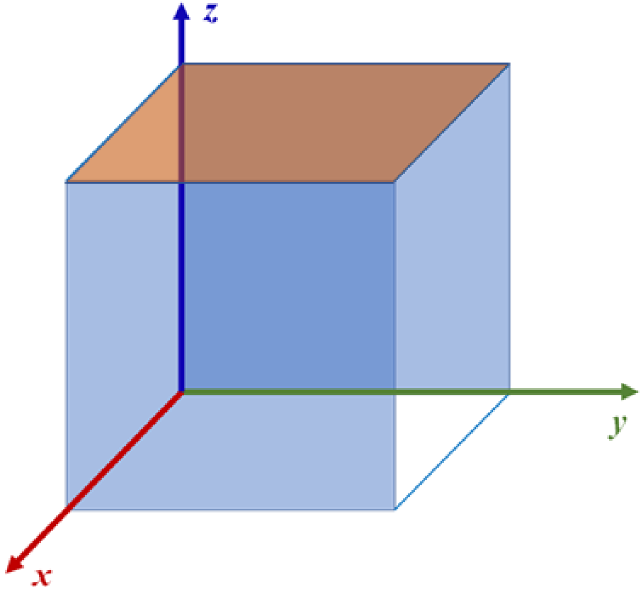


Miller indices ------ (Faces of a cube)

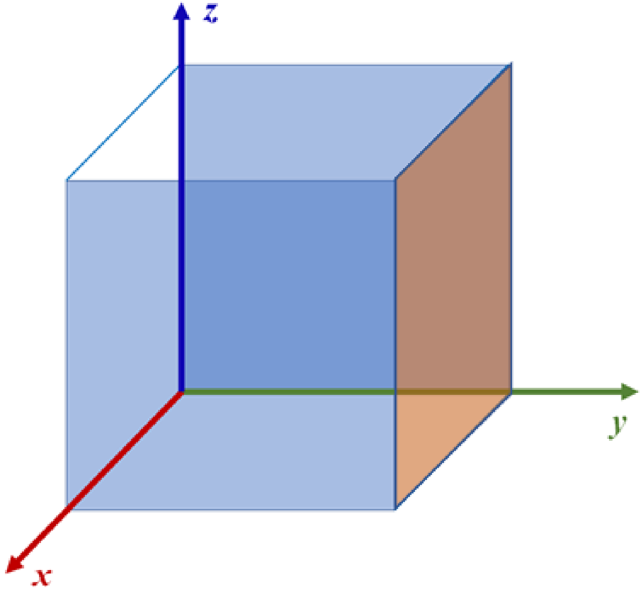


Intercepts	1	∞	∞
Reciprocals	$\frac{1}{1}$	$\frac{1}{\infty}$	$\frac{1}{\infty}$
Plane	(100)		

Why do we not directly use the intercept form?



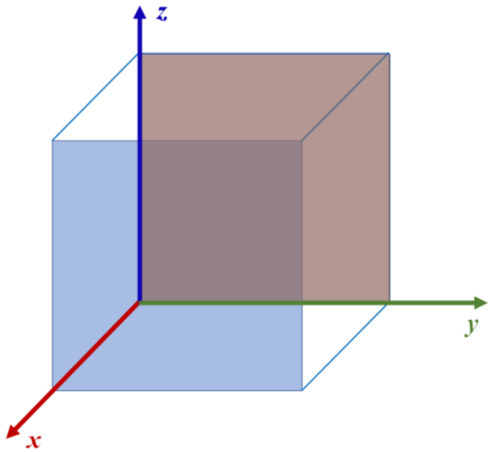
Intercepts	∞	∞	1
Reciprocals	$\frac{1}{\infty}$	$\frac{1}{\infty}$	$\frac{1}{1}$
Plane	(001)		



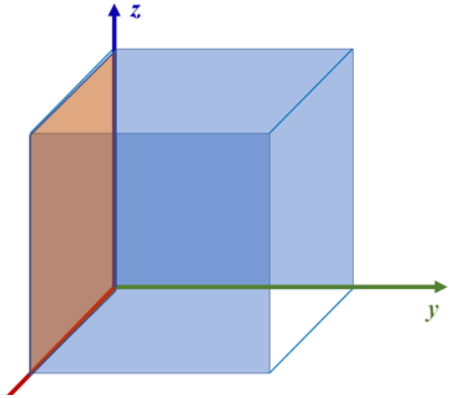
Intercepts	∞	1	∞
Reciprocals	$\frac{1}{\infty}$	$\frac{1}{1}$	$\frac{1}{\infty}$
Plane	(010)		

- Are these all equivalent planes ?
- Family of planes {100} --------- 6 in a cubic unit cell
- 4-fold rotational symmetry along the face normal.

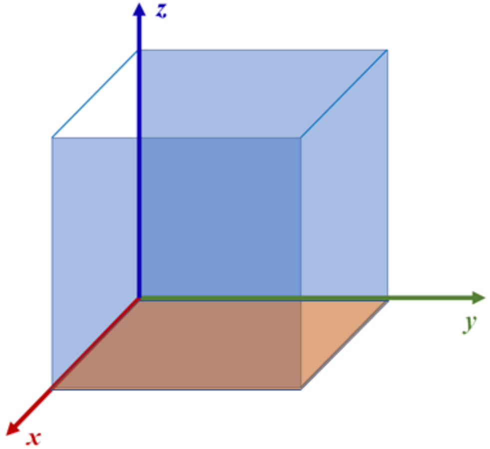
A set of planes related by symmetry operations of the lattice or the crystal is called a family of planes.



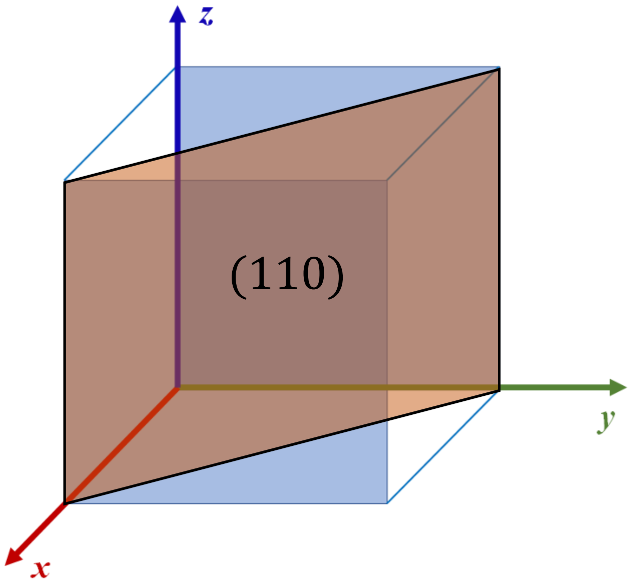
$(\bar{1}00)$

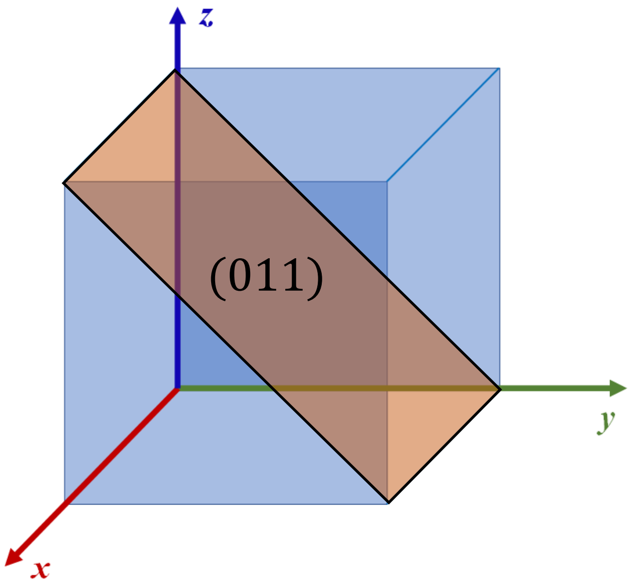


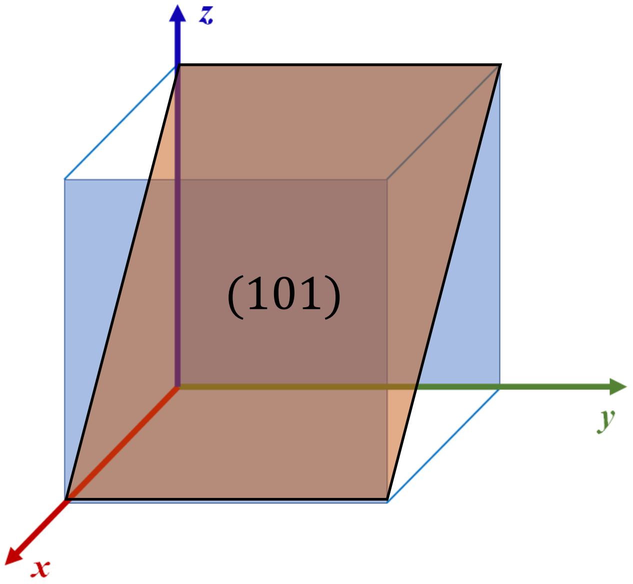
$(0\bar{1}0)$



$(00\bar{1})$

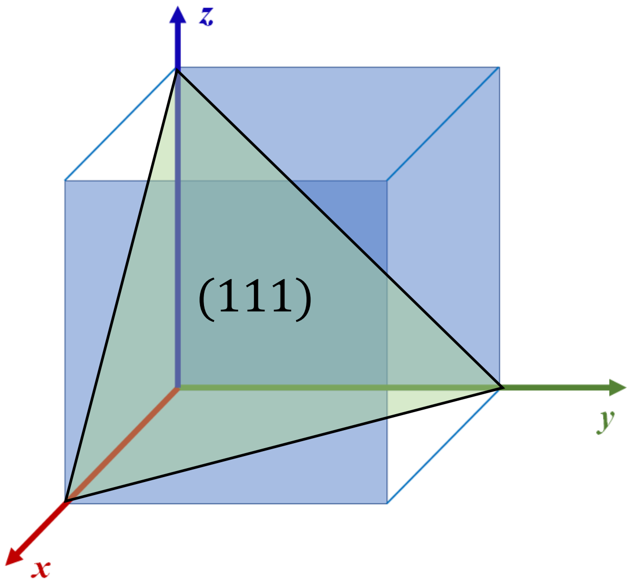


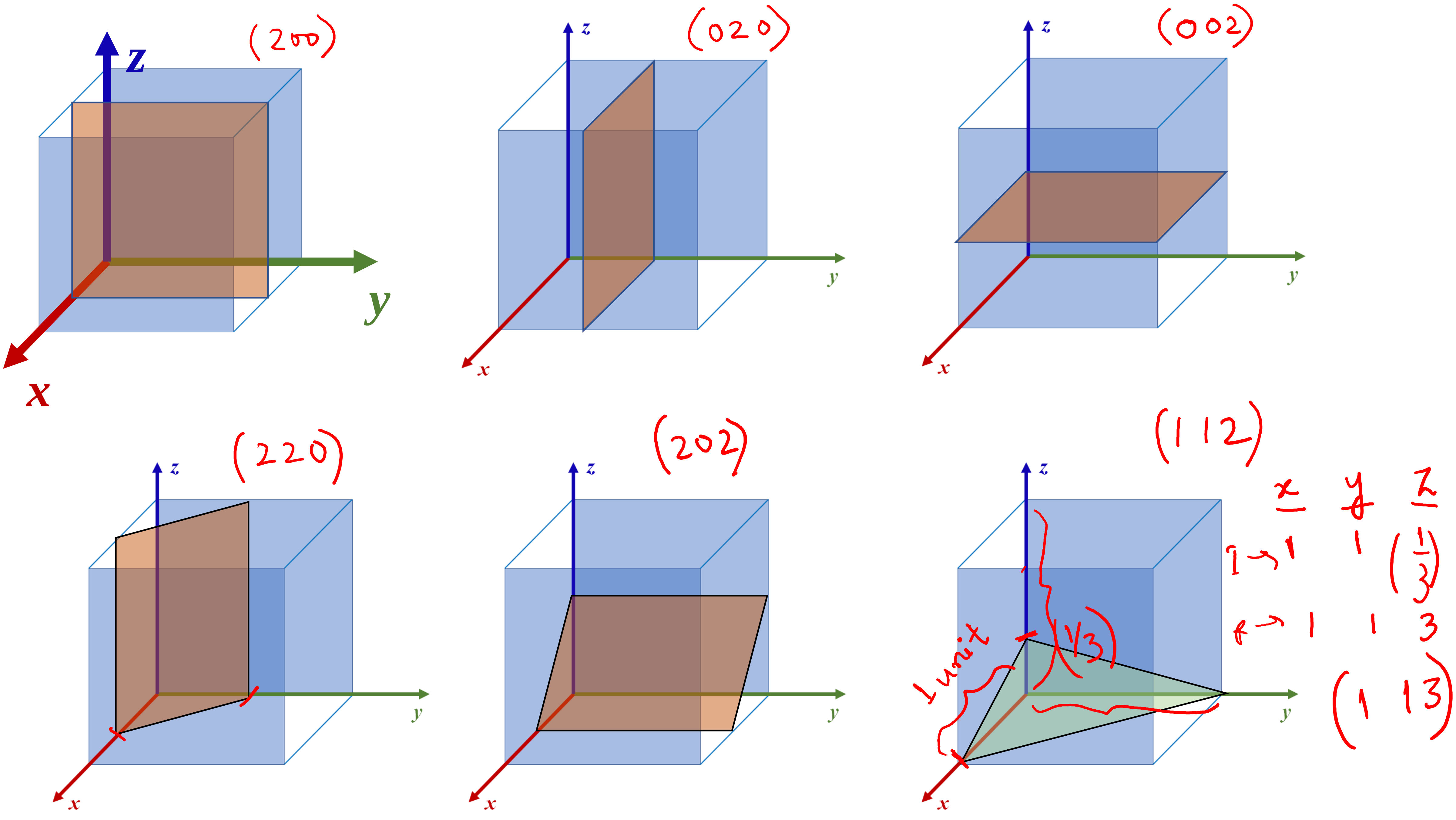




Intercepts	1	1	∞
Reciprocals	$\frac{1}{1}$	$\frac{1}{1}$	$\frac{1}{\infty}$
Plane		(110)	

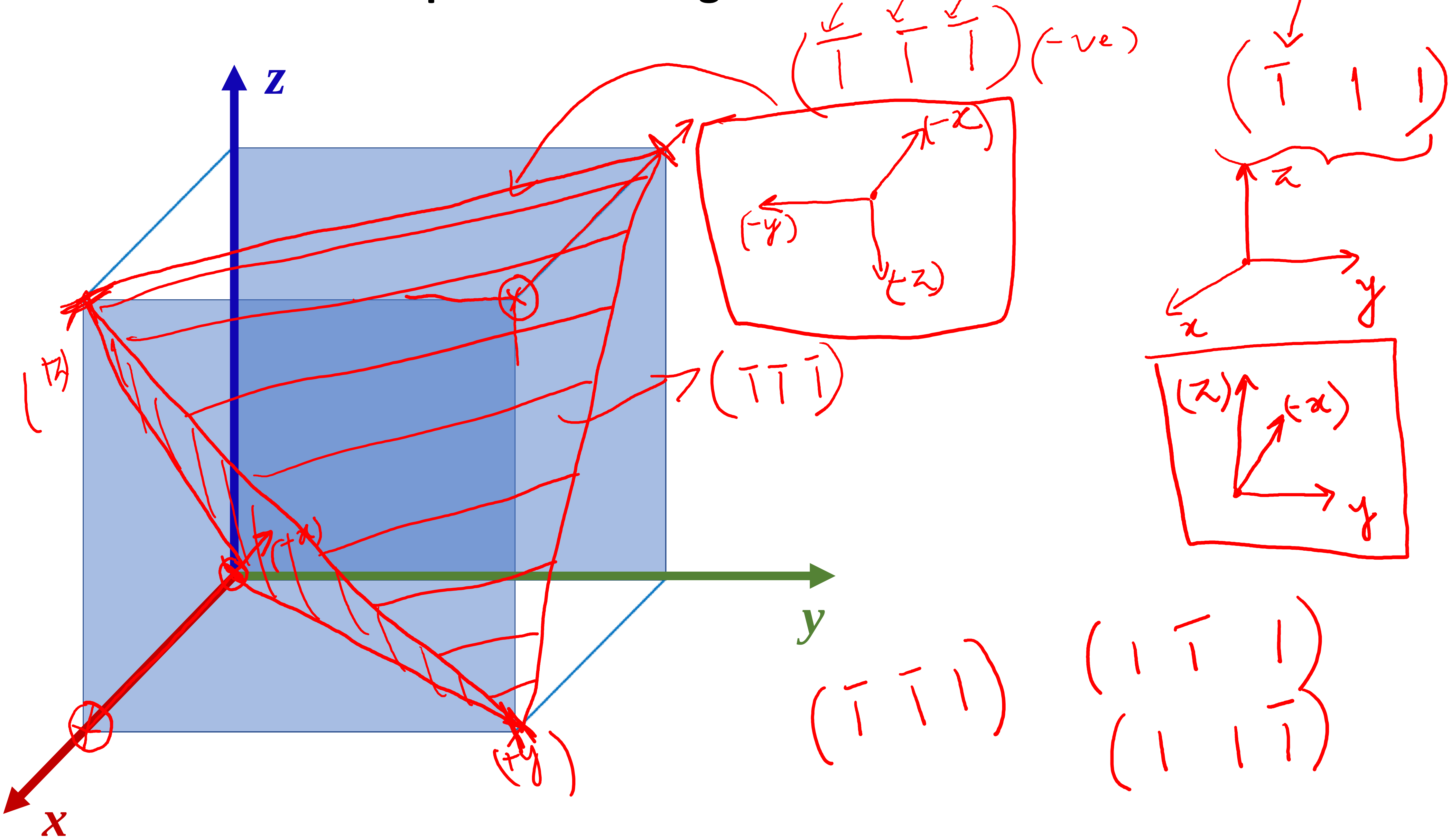
- Family of planes {110} --------- 6 in a cubic unit cell
- Family of planes {111} --------- 8 in a cubic unit cell





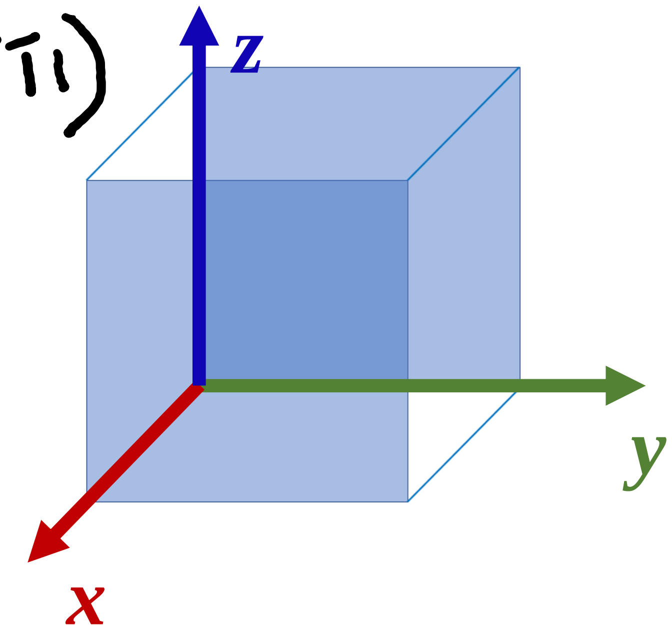
z
y
x
(200)
(020)
(002)
(220)
(202)
(112)
x y z
1 1 (1/3)
1 1 3
(1 1 3)
1 unit
1/3

How do we draw a lattice plane with negative indices?

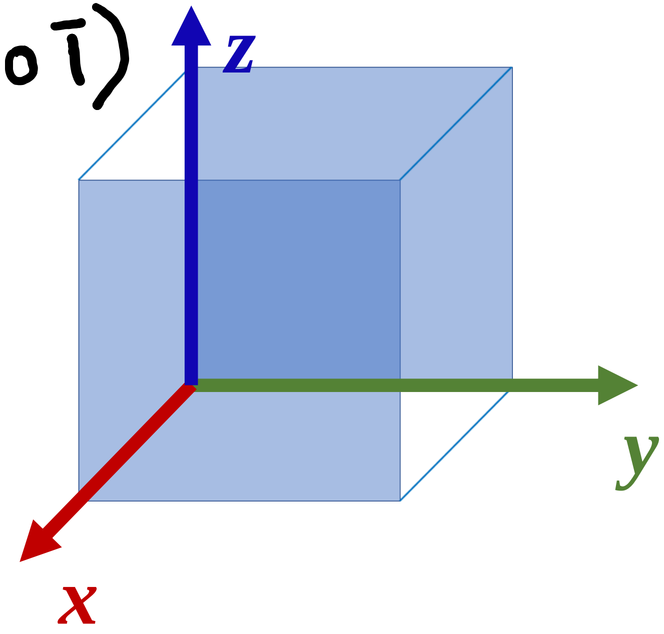


How do we construct the lattice planes with the given Miller indices?

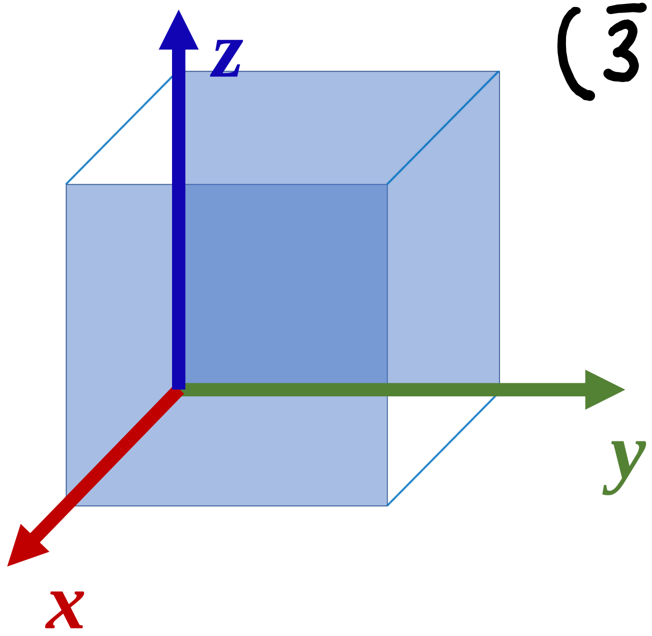
$(\bar{1}\bar{1}1)$



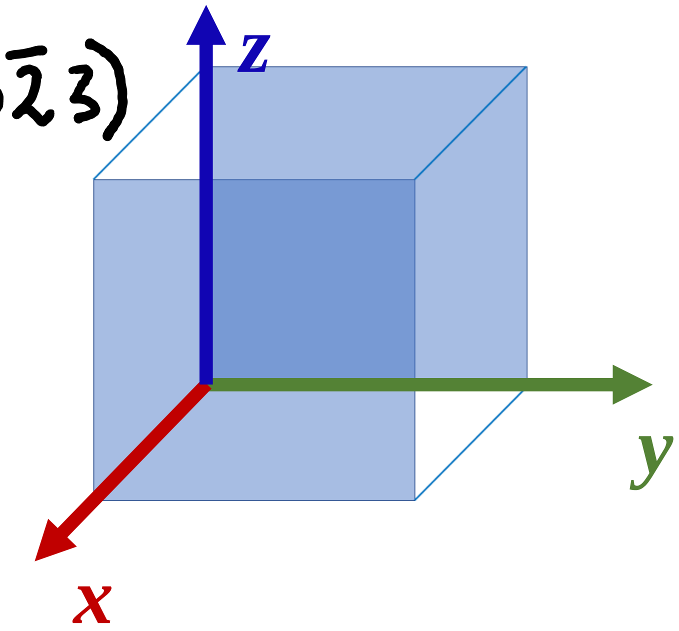
$(20\bar{1})$



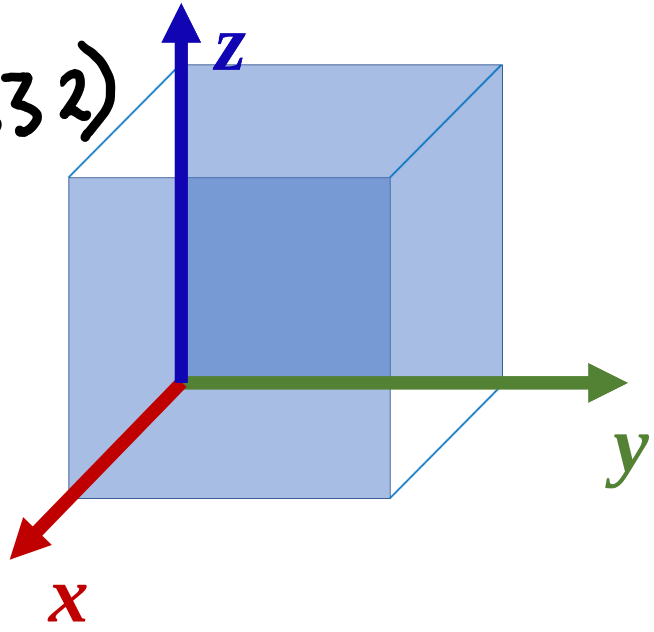
$(\bar{3}2\bar{1})$



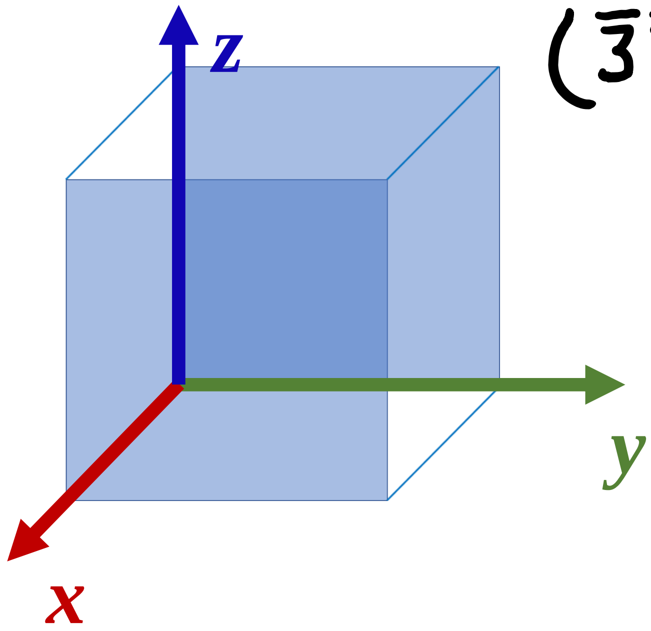
$(0\bar{2}3)$

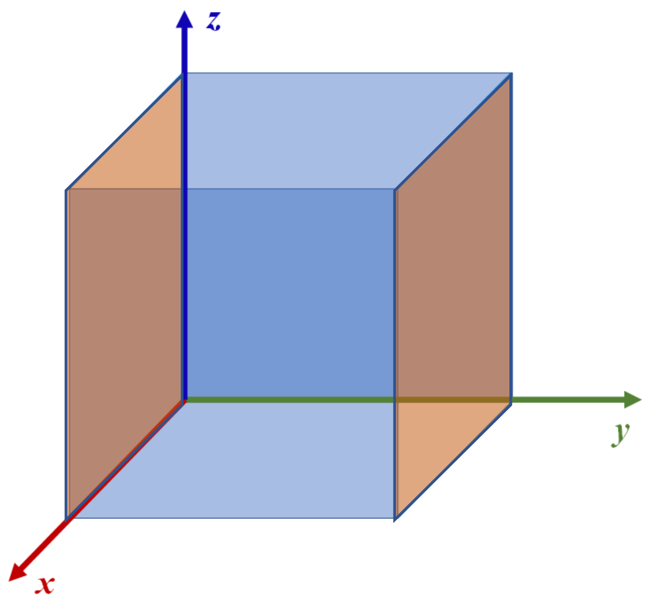


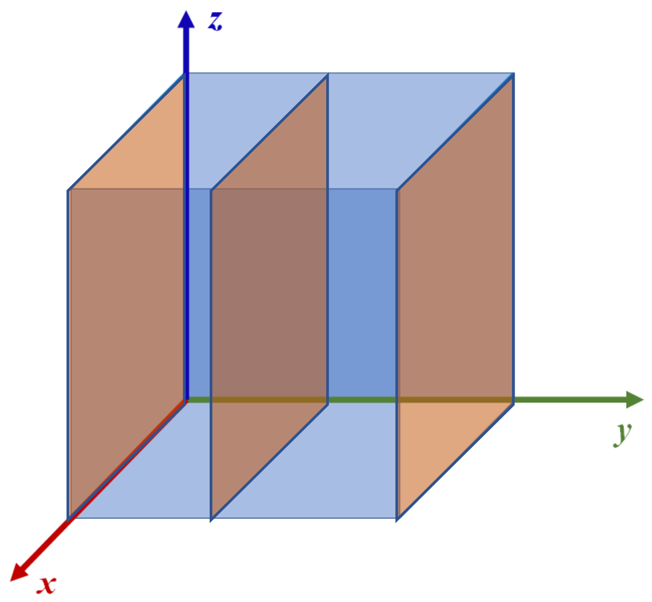
$(\bar{2}32)$



$(\bar{3}\bar{3}\bar{1})$







- Higher the indices are, smaller is the distance between the two adjacent planes.

- Distance between two lattice planes:
  Interplanar distance (d-spacing)

$$\boxed{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} = \frac{1}{(d_{hkl})^2}}$$

$$\boxed{d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}}$$

Volume and interplanar spacing

The following equations give the volume V of the unit cell.

Cubic: $$V = a^3$$

Tetragonal: $$V = a^2c$$

Hexagonal: $$V = \frac{\sqrt{3}\,a^2c}{2} = 0.866a^2c$$

Rhombohedral: $$V = a^3\sqrt{1 - 3\cos^2\alpha + 2\cos^3\alpha}$$

Orthorhombic: $$V = abc$$

Monoclinic: $$V = abc\sin\beta$$

Triclinic: $$V = abc\sqrt{1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma}$$

Interplanar spacing

The spacing d between adjacent (hkl) lattice planes is given by:

- Cubic:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

- Tetragonal:

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

- Hexagonal:

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$$

- Rhombohedral:

$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2)\sin^2\alpha + 2(hk + kl + hl)(\cos^2\alpha - \cos\alpha)}{a^2(1 - 3\cos^2\alpha + 2\cos^3\alpha)}$$

- Orthorhombic:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

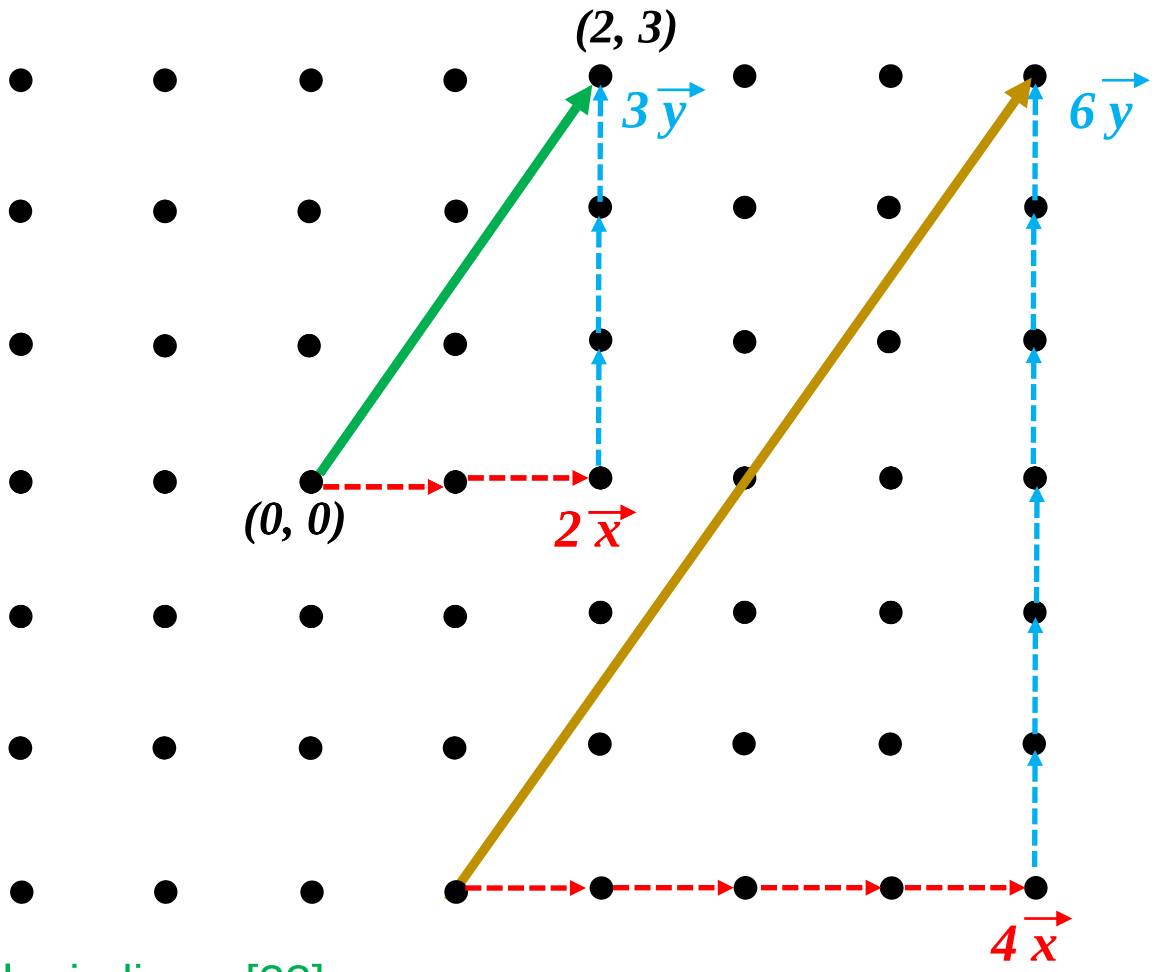
- Monoclinic:

$$\frac{1}{d^2} = \left(\frac{h^2}{a^2} + \frac{k^2\sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right)\csc^2\beta$$

- Triclinic:

$$\frac{1}{d^2} = \frac{\frac{h^2}{a^2}\sin^2\alpha + \frac{k^2}{b^2}\sin^2\beta + \frac{l^2}{c^2}\sin^2\gamma}{1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma}$$

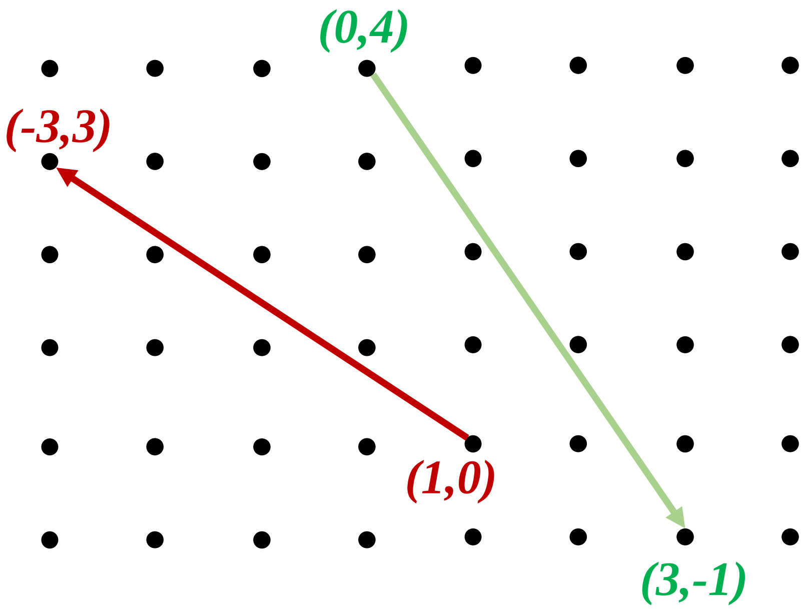
Miller indices for directions in 2-D



Miller indices: [23]

Miller indices: [4 6] ≈ 2 [2 3]

- Does the miller index for a direction necessarily start and end at distinct lattice points?



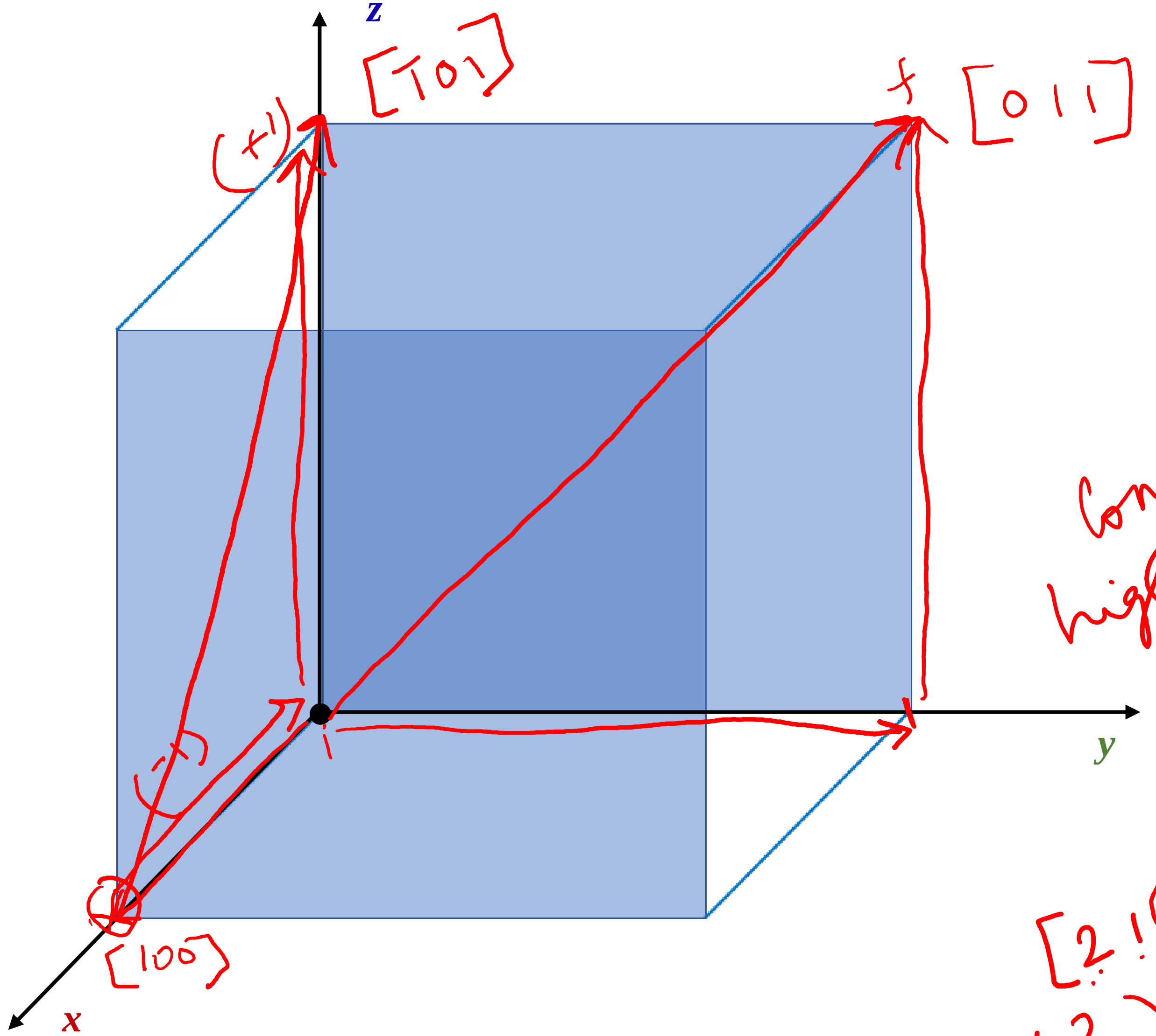
How to draw a direction if Miller indices are given?

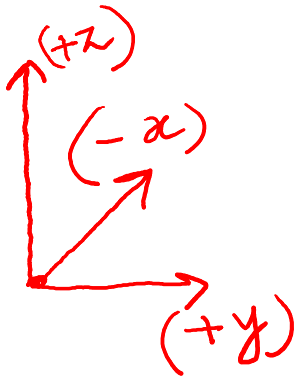
[100]

[011]

[$\bar{1}$01]

[$\bar{2}$13]





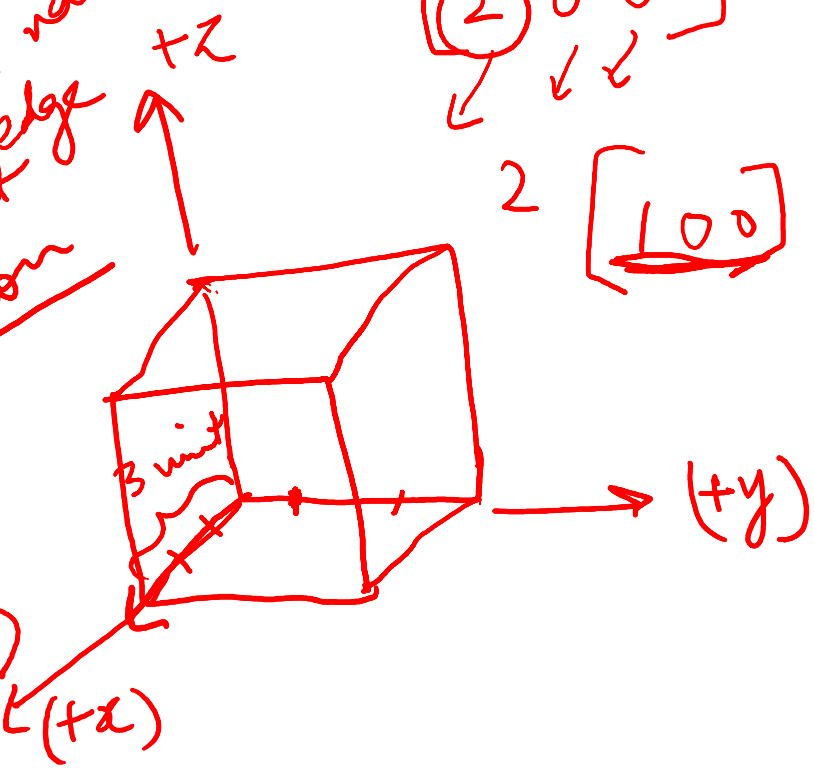
Consider the highest index value as your unit edge Direction

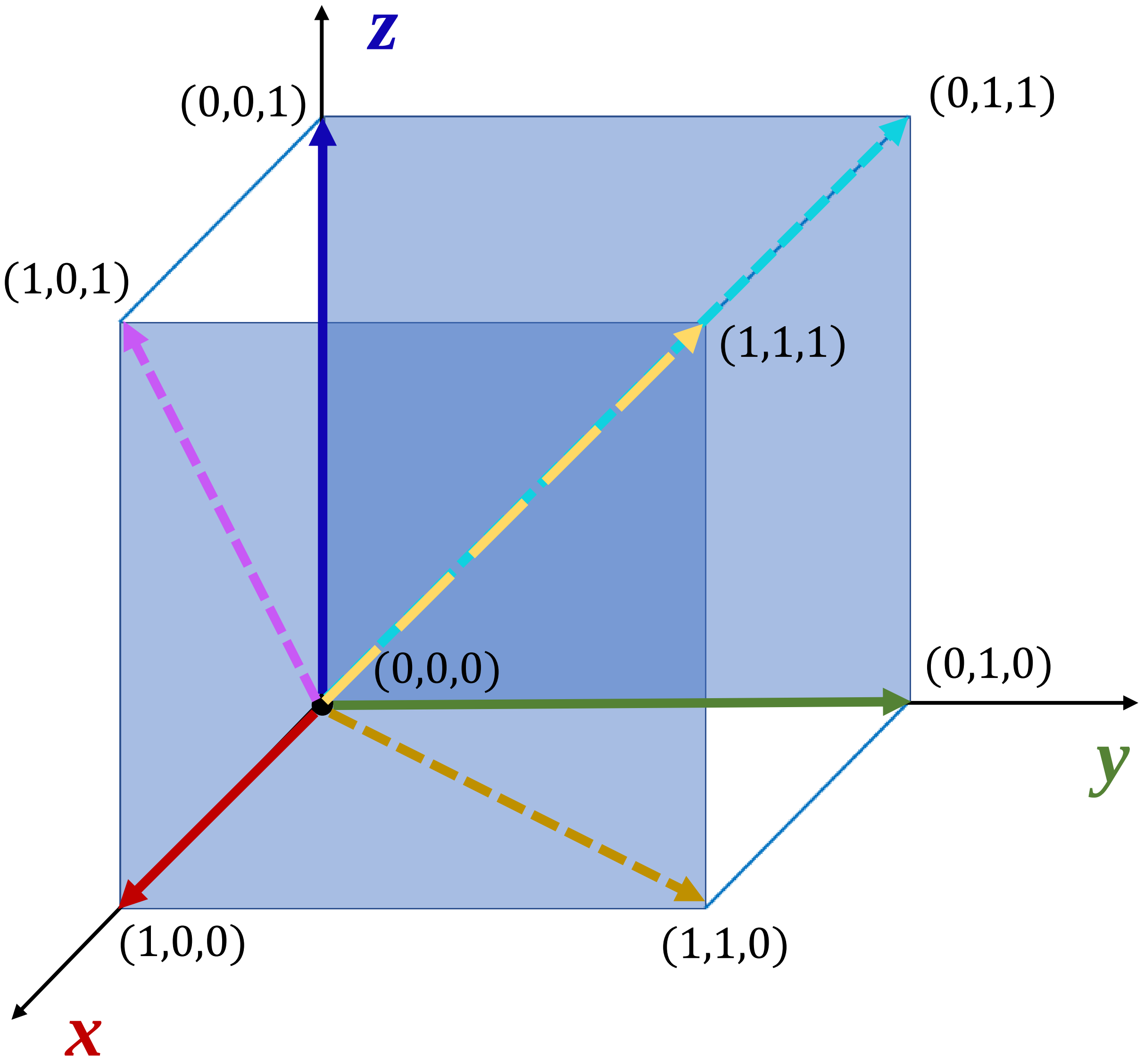
[2 0 0]

2 [1 0 0]

[2 1 3]

$\left(\frac{2}{3}\right) \left(\frac{1}{3}\right) \left(\frac{3}{3}\right)$





[1 0 0]
[0 1 0]
[0 0 1]

Family of directions: <1 0 0>

[1 1 0]
[0 1 1]
[1 0 1]

Face diagonals
Family of directions: <1 1 0>

[1 1 1]

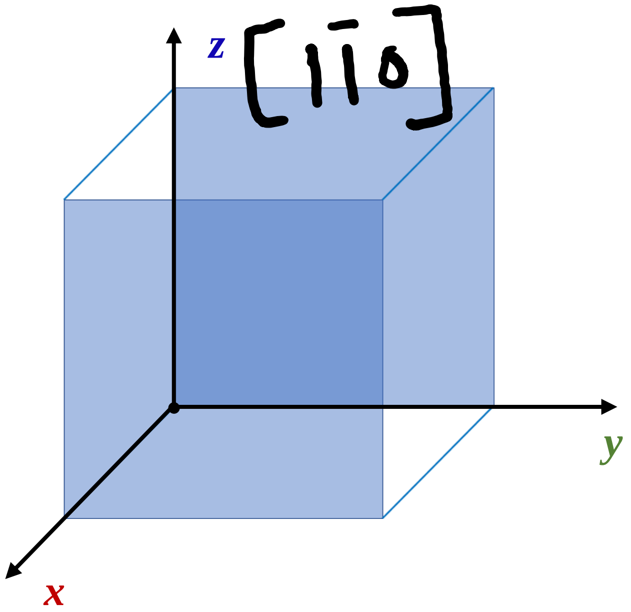
Body diagonal

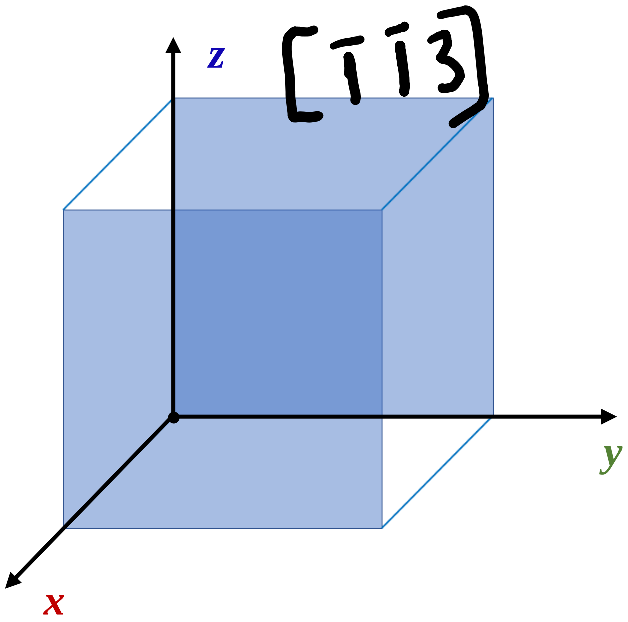
Family of directions

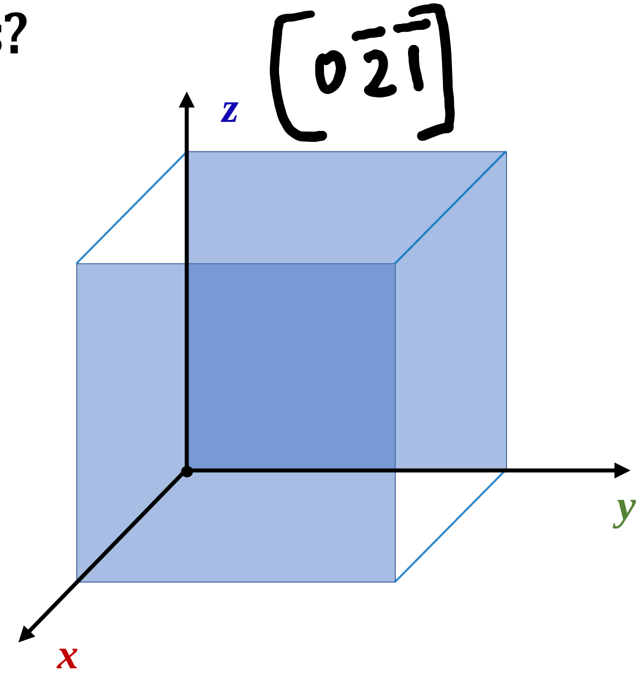
Index	Members in family for cubic lattices	Number
<100>	$[100],[\bar{1}00],[0\bar{1}0],[001],[00\bar{1}]$	3 x 2 = 6
<110>	$[110],[\bar{1}10],[1\bar{1}0],[\bar{1}\bar{1}0],[101],[\bar{1}01],[10\bar{1}],[\bar{1}0\bar{1}],[011],[0\bar{1}1],[01\bar{1}],[0\bar{1}\bar{1}]$	6 x 2 = 12
<111>	$[111],[\bar{1}11],[1\bar{1}1],[11\bar{1}],[\bar{1}\bar{1}1],[\bar{1}1\bar{1}],[1\bar{1}\bar{1}],[\bar{1}\bar{1}\bar{1}]$	4 x 2 = 8

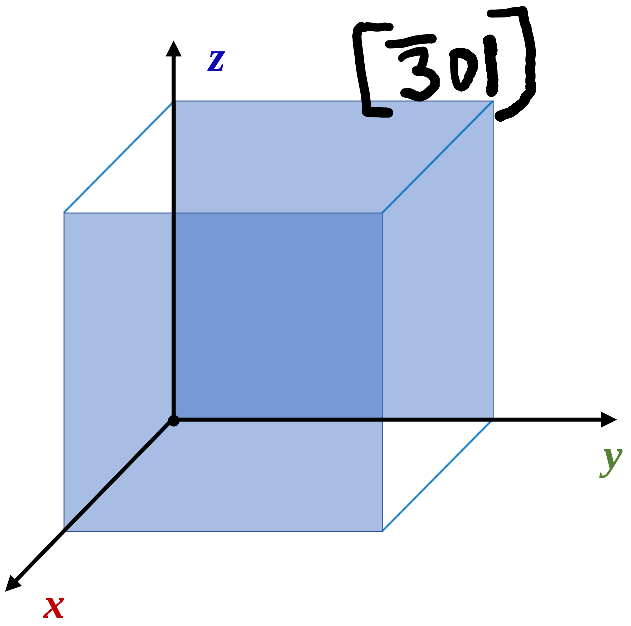
Symbol	Alternate symbol		
[ ]		→	Particular direction
< >	[[ ]]	→	Family of directions

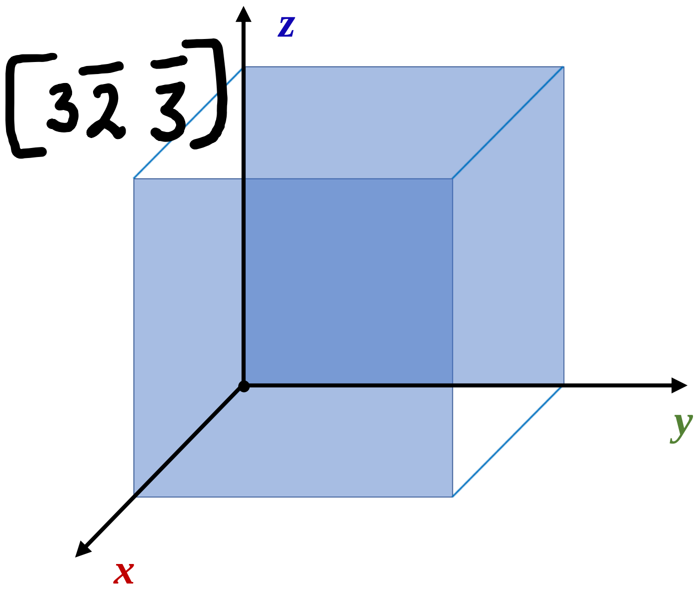
How do we construct the lattice directions with the given Miller indices?

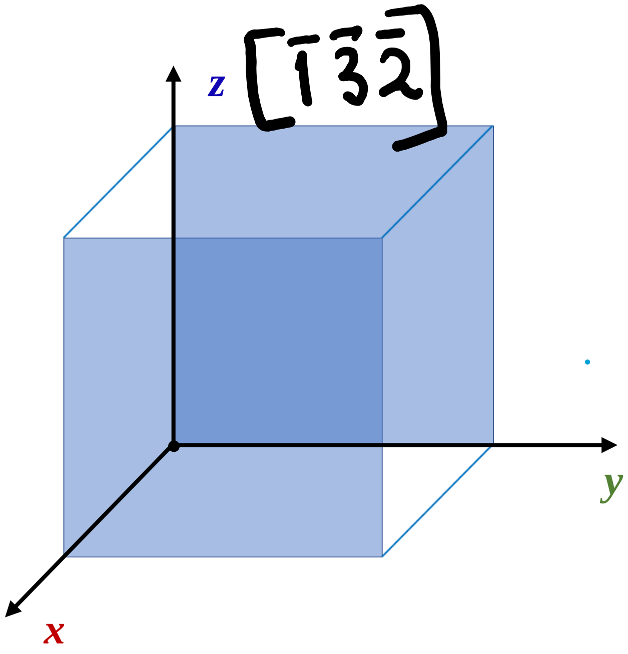


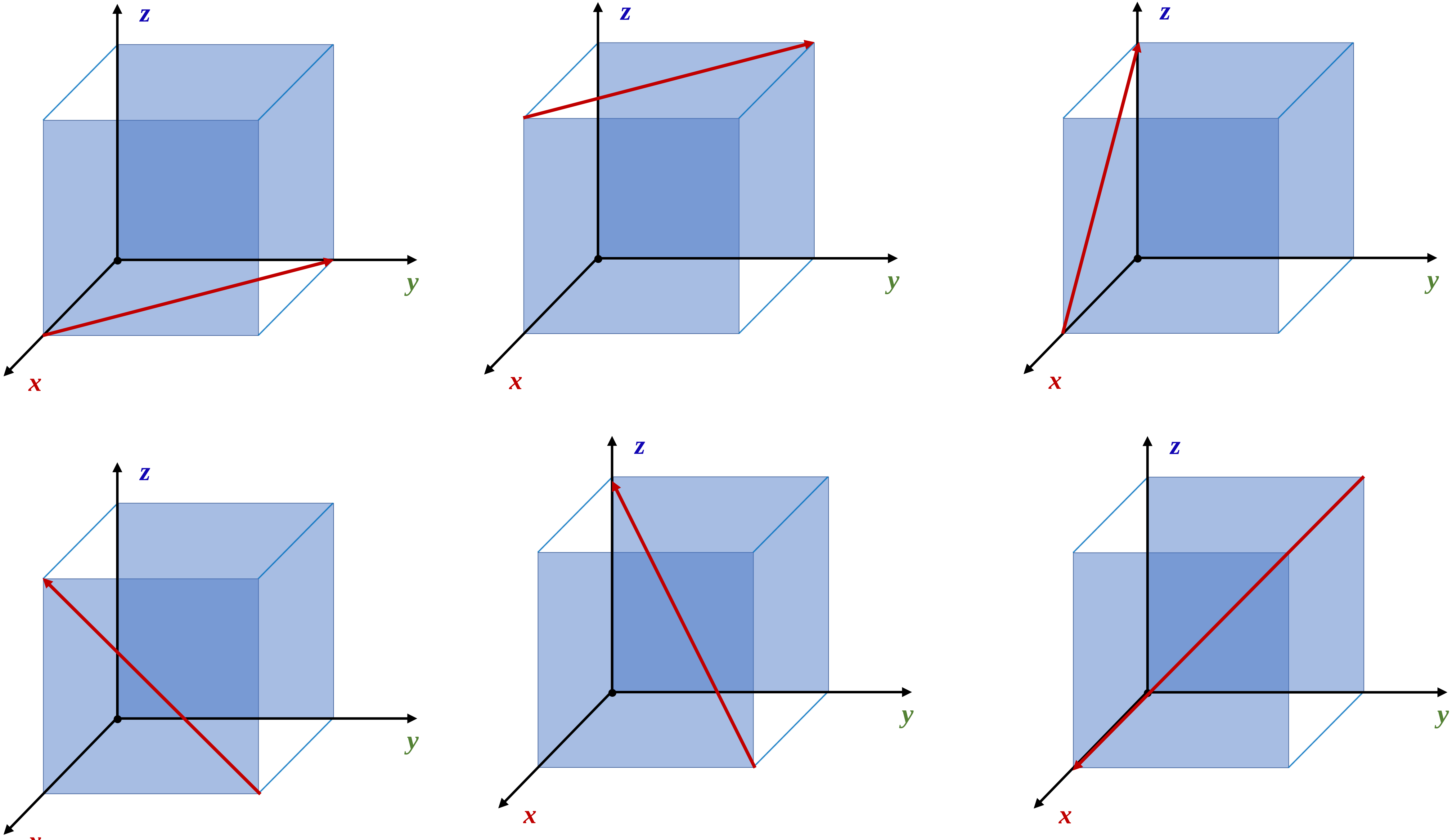











z
y
x
z
y
x
z
y
x
z
y
x
z
y
x
z
y
x

MLL 100

Introduction to Materials Science and Engineering

Lecture-6

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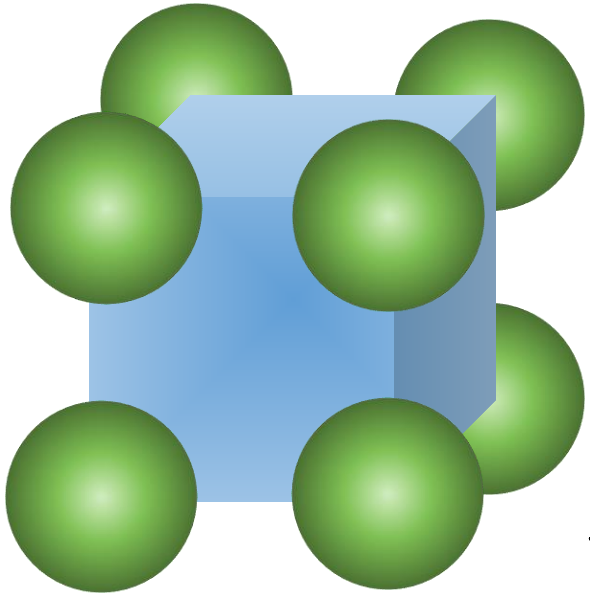
IIT Delhi
Department of Materials Science and Engineering

What we learnt in Lecture-5?

- Miller indices in cubic system

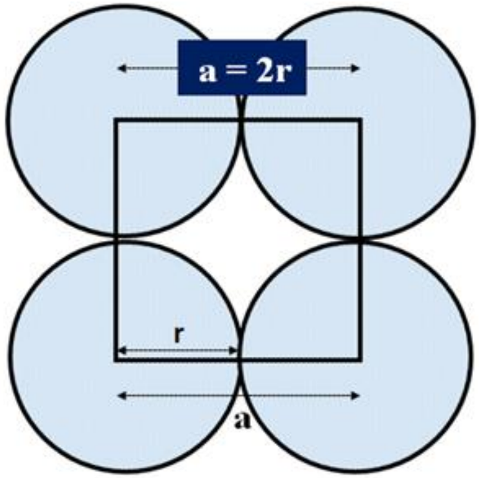
Atomic packing factor (APF): Simple Cubic



$\longleftarrow a \longrightarrow$

Let the radius of an atom be and the lattice parameter of the cubic cell be 'a'.

$\therefore$ If you consider (100); two atoms will be in contact along the edges (as shown in the figure)

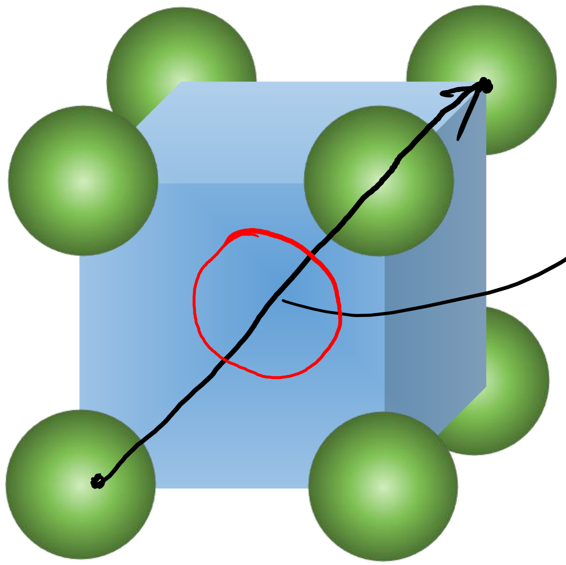


$\therefore 2r = a \quad \therefore r = \left(a/2\right)$

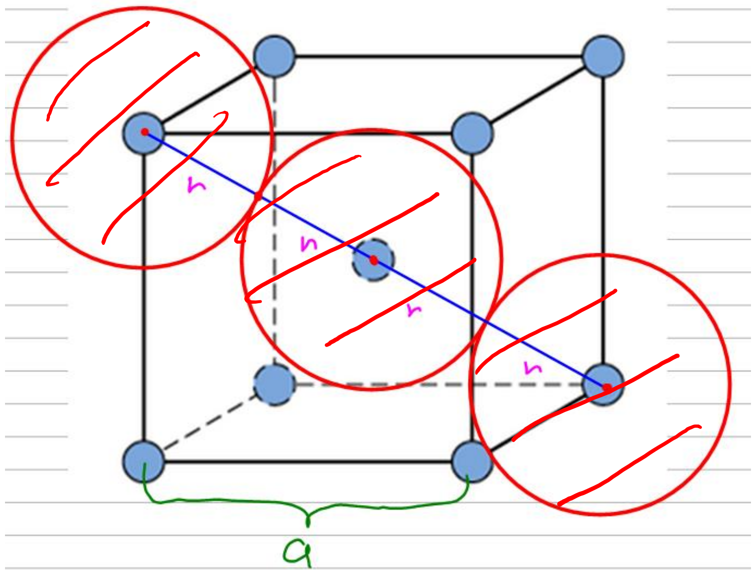
$$\therefore APF = \frac{(\text{No. of effective atoms (UC)}) \times \text{Vol. of an atom}}{\text{Vol. of a UC}}$$

$$\therefore APF = \frac{1 \times \frac{4}{3}\pi r^3}{a^3} = 52\%$$

Atomic packing factor (APF): Body-centred cubic



[The atoms will be most closely packed along the body diagonal, ie; [1 1 1].

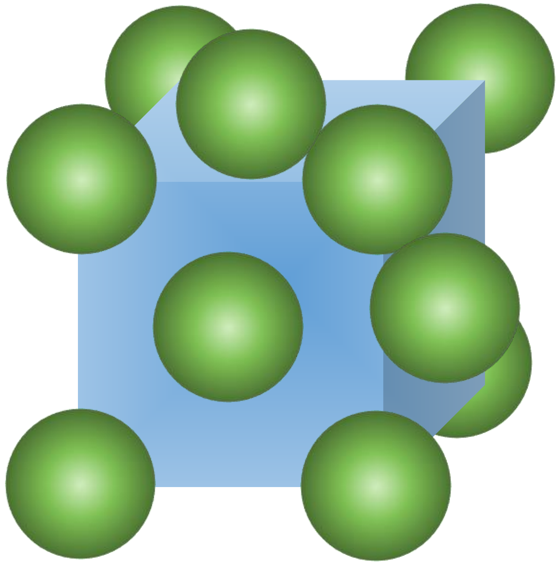


$\therefore 4r = \sqrt{3}a$

$r = \left(\frac{\sqrt{3}a}{4}\right)$

Similarly, APF $= \dfrac{2 \times \frac{4}{3}\pi\left(\frac{\sqrt{3}}{4}a\right)^3}{a^3} = \underline{\underline{68\%}}$

Atomic packing factor (APF): Face-centred cubic

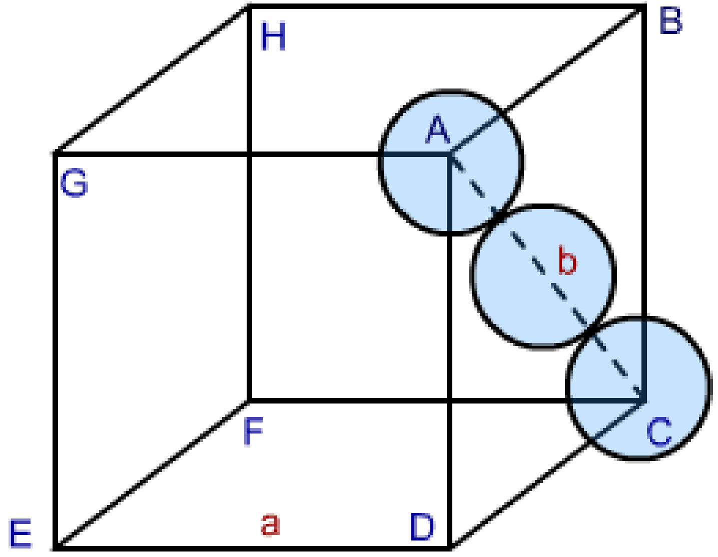


In FCC, the atoms will be closely packed along the face diagonals.

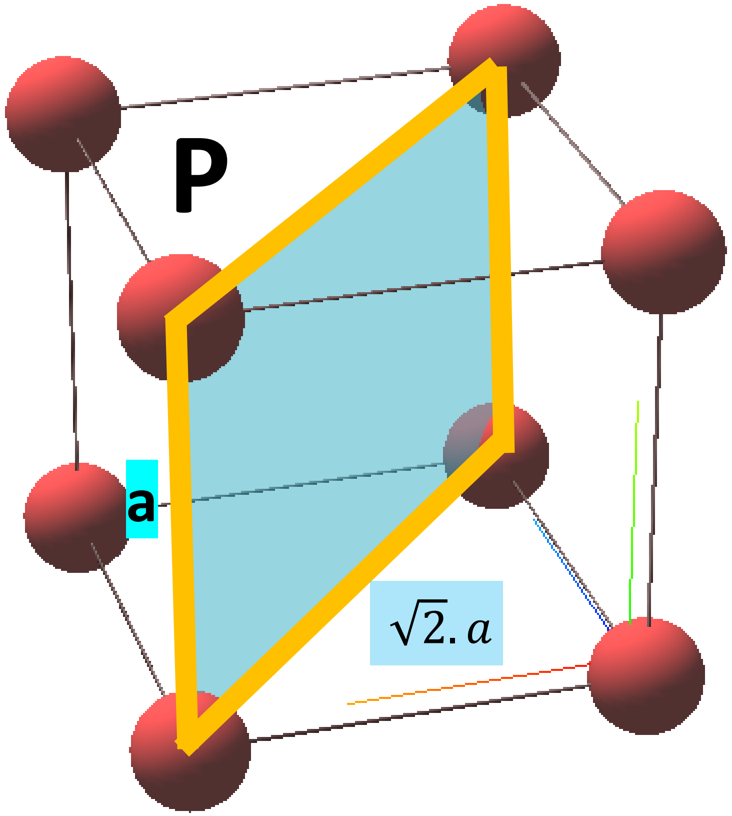
$$\therefore 4r = \sqrt{2}a \quad \therefore r = \left(\frac{\sqrt{2}a}{4}\right)$$

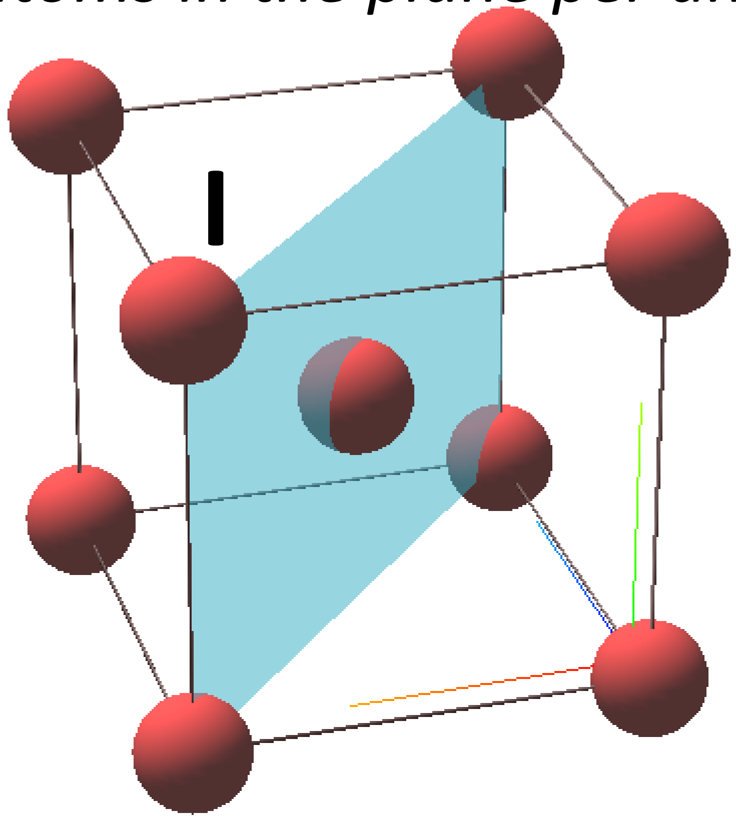
$$\therefore APF = \frac{4 \times \frac{4}{3}\pi\left(\frac{\sqrt{2}a}{4}\right)^3}{a^3}$$

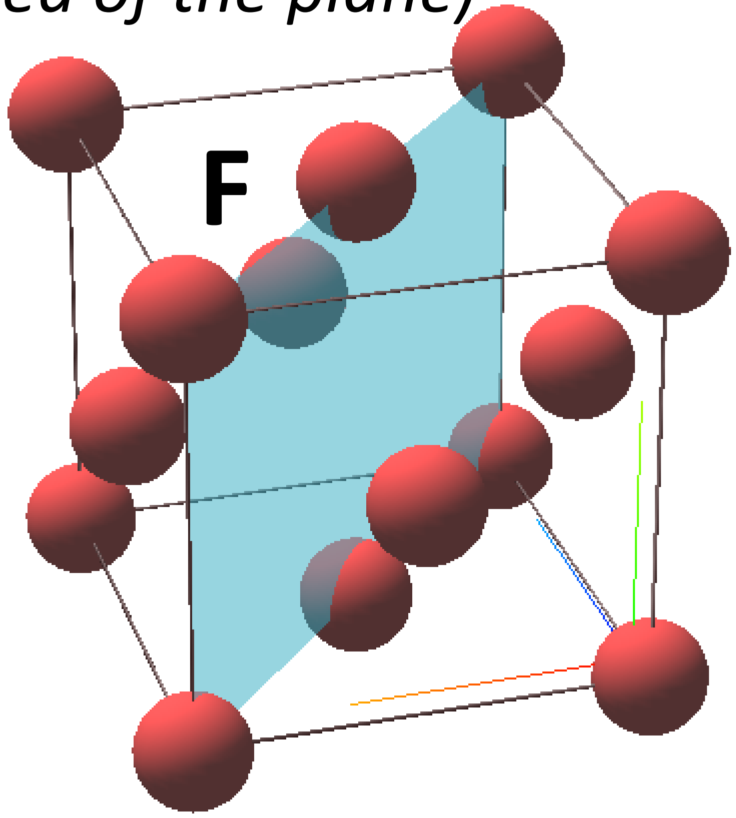
$$= \underline{\underline{74\%}}.$$



Planar density *(No. of atoms in the plane per unit area of the plane)*







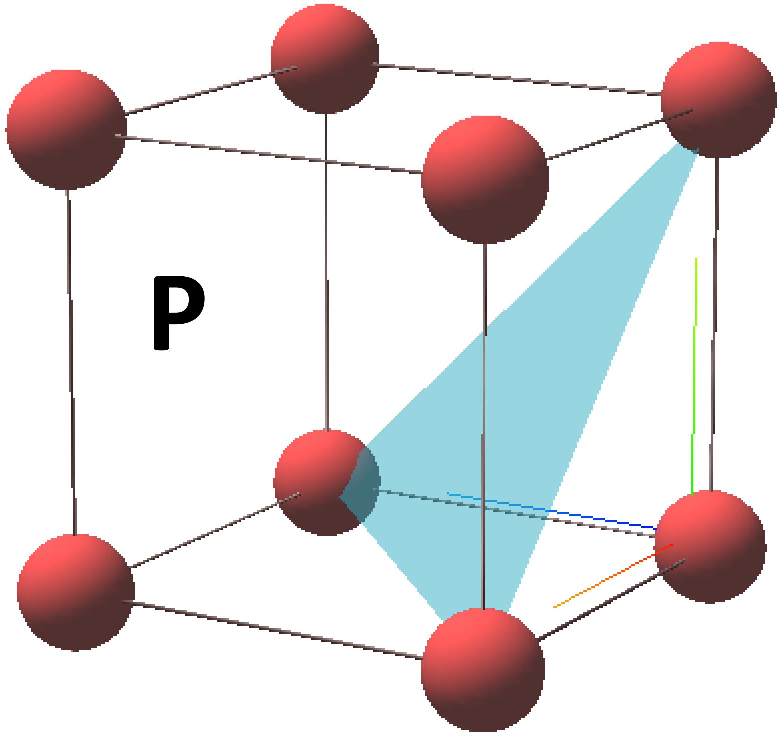
$(4)\ \mathrm{x}\,\frac{1}{4} = 1$

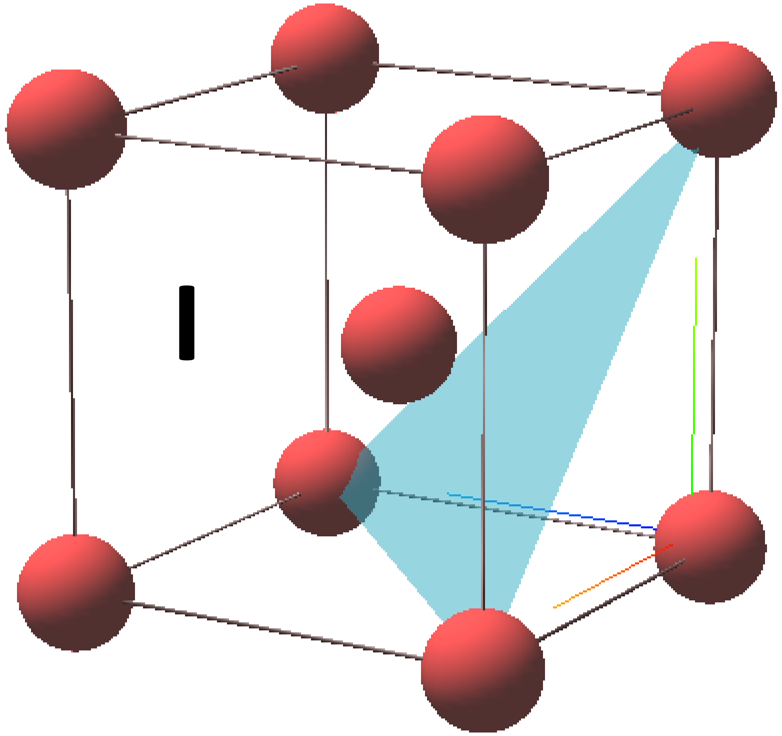
$[(4)\ \mathrm{x}\,\frac{1}{4}] + [(1)x\ 1] = 2$

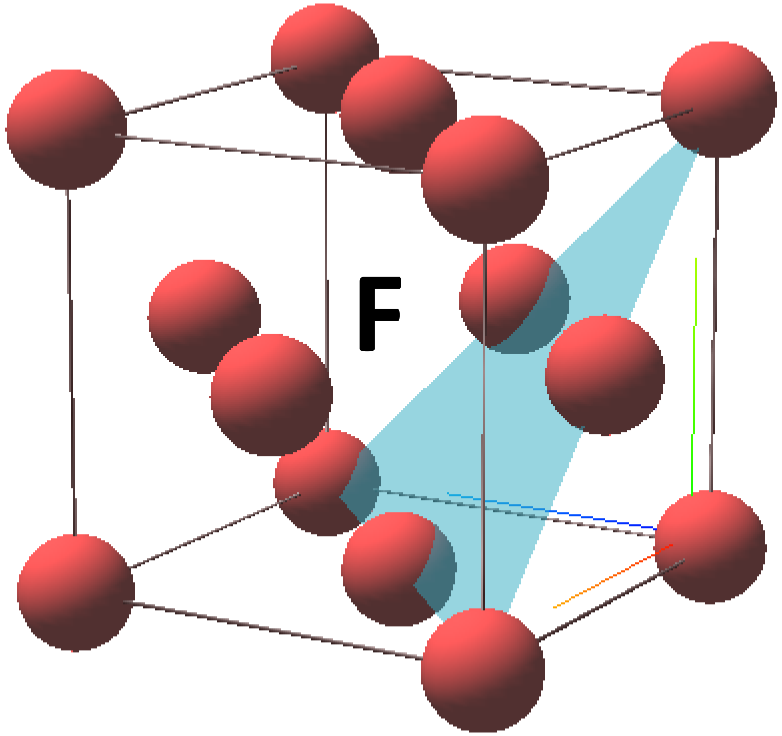
$[(4)\ \mathrm{x}\,\frac{1}{4}] + [(2)x\,\frac{1}{2}] = 2$

Area of (110) plane = a x $(\sqrt{2}.a)$ = $\sqrt{2}$. a^2

Which of the cubic Bravais lattice has the highest packing density for the (1 1 1) plane?







$(3)\ \mathrm{x}\,\frac{1}{6} = \frac{1}{2}$

$(3)\ \mathrm{x}\,\frac{1}{6} = \frac{1}{2}$

$[(3)\ \mathrm{x}\,\frac{1}{6}] + [(3)x\,\frac{1}{2}] = 2$

Area of (111) plane = $(\sqrt{3}/4.\,a^2)$ = $(\sqrt{3}/4.\,(\sqrt{2}a)2)$ = 0.866 a^2

Weiss Zone law

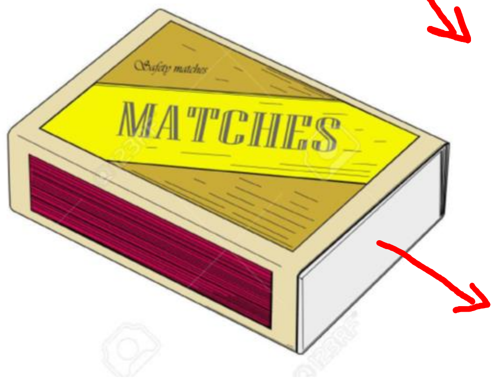
If a (h k l) plane lies in a zone [u v w] --------> if the [u v w] direction is || to the (h k l) plane, then:

$$(hu + kv + lw) = 0$$

- ❑ Zone: a set of planes in a crystal whose intersections are all parallel.
- ❑ Zone axis: Common direction of the intersections.

- ❑ Can the directions in a crystal be called zone axes?

  …… 'Zone axes' and 'directions' are synonymous.

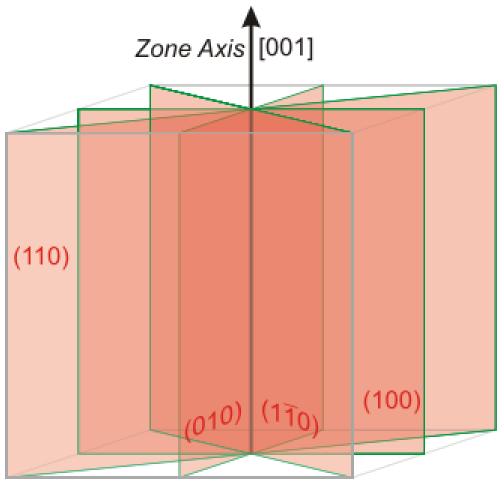


- ❑ Direction of a Pencil lead: Zone axis for all the faces enclosing it.

Zone axis at the intersection of the lattice planes

- If (h_1 k_1 l_1) & (h_2 k_2 l_2) are two planes having a common direction [u v w], according to Weiss zone law:

$$u.h_1 + v.k_1 + w.l_1 = 0 \ \& \ u.h_2 + v.k_2 + w.l_2 = 0$$

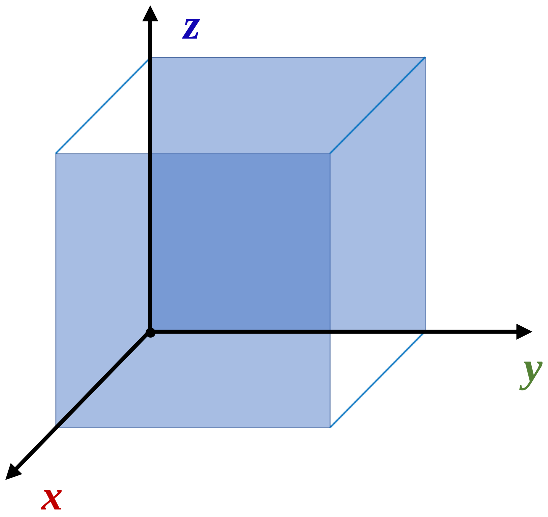


$$\begin{bmatrix} u & v & w \\ h_1 & k_1 & l_1 \\ h_2 & k_2 & l_2 \end{bmatrix} = 0$$

$$\therefore \quad u = (k_1 l_2 - k_2 l_1)$$

$$v = -(h_1 l_2 - l_1 h_2)$$

$$w = (h_1 k_2 - h_2 k_1)$$



Lattice plane parallel to the two directions

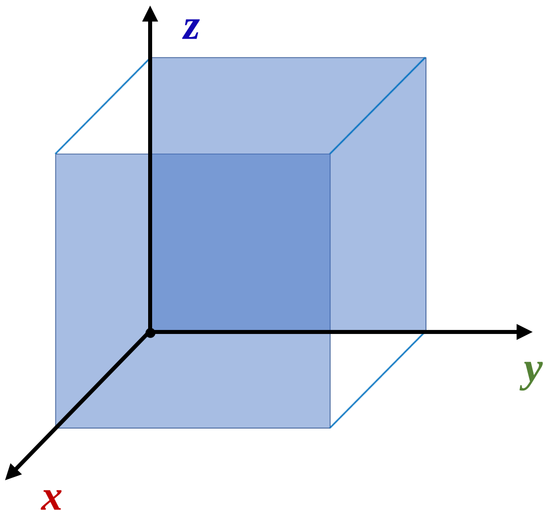
$(h\,k\,l)$ $\qquad\qquad$ $\underbrace{[u_1\ v_1\ w_1] \text{ and } [u_2\ v_2\ w_2]}$

$$\therefore \begin{bmatrix} h & k & l \\ u_1 & v_1 & w_1 \\ u_2 & v_2 & w_2 \end{bmatrix} = 0$$

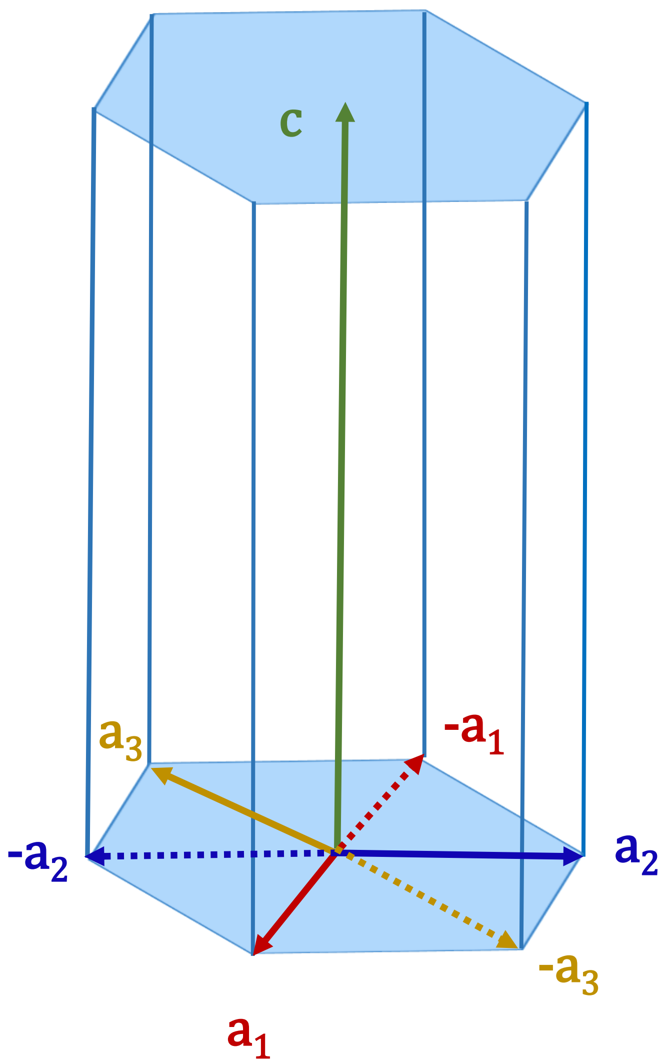
$$\therefore h = (v_1 w_2 - v_2 w_1)$$

$$k = -(u_1 w_2 - u_2 w_1)$$

$$l = (u_1 v_2 - u_2 v_1)$$



Miller-Bravais indices for hexagonal system

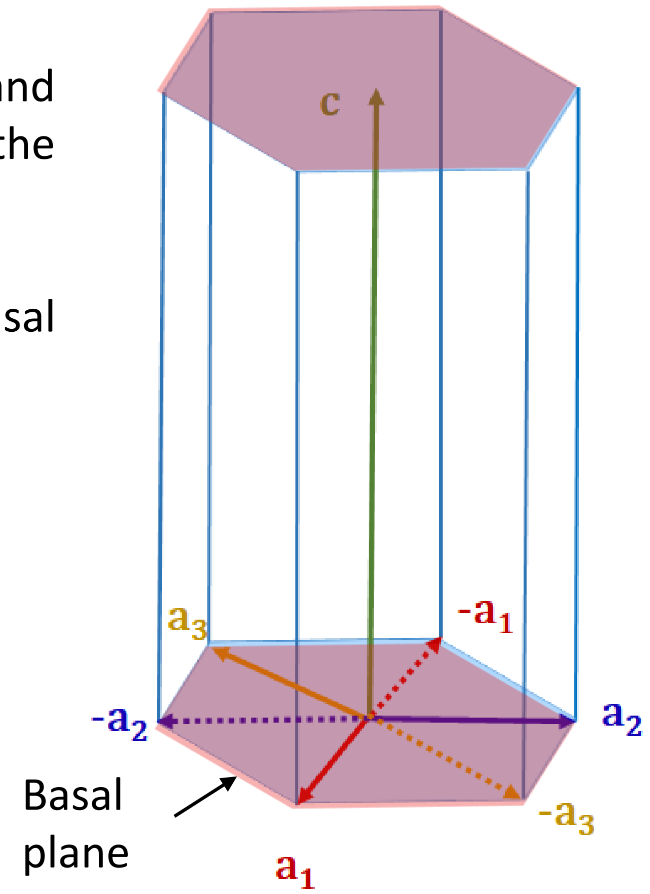


h	k	i	l
↓	↓	↓	↓
a_1	a_2	a_3	c

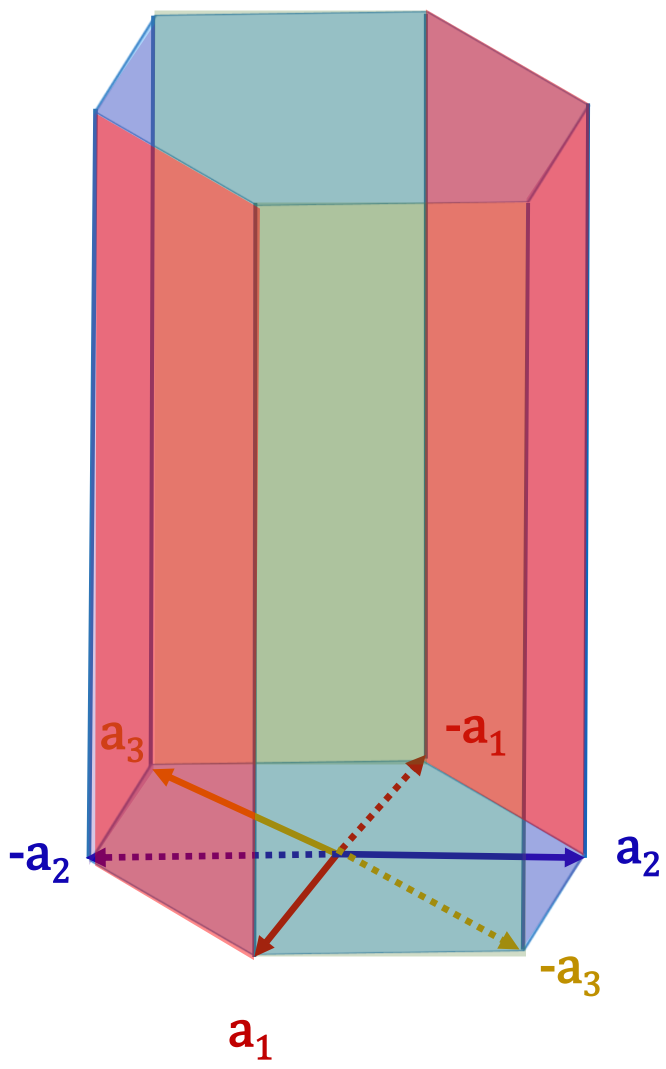
$$i = -(h + k)$$

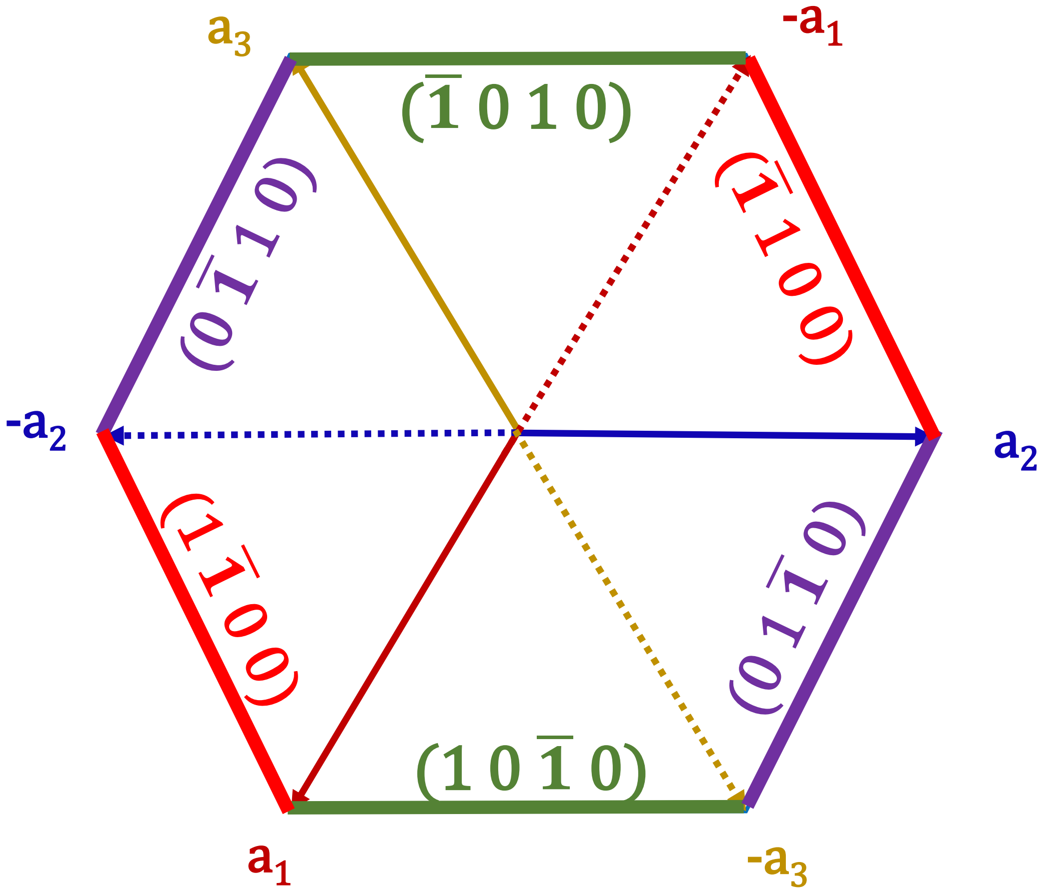
- a_1, a_2 and a_3 are three close-packed directions and are coplanar, lying on the basal plane of the crystal. These axes are at 120° w.r.t each other.
- Fourth axis, c-axis, is perpendicular to the basal plane.
- a_3-axis is the redundant axis.

Intercepts	∞	∞	∞	1
Reciprocals	$\frac{1}{\infty}$	$\frac{1}{\infty}$	$\frac{1}{\infty}$	$\frac{1}{1}$
Plane	(0001)			



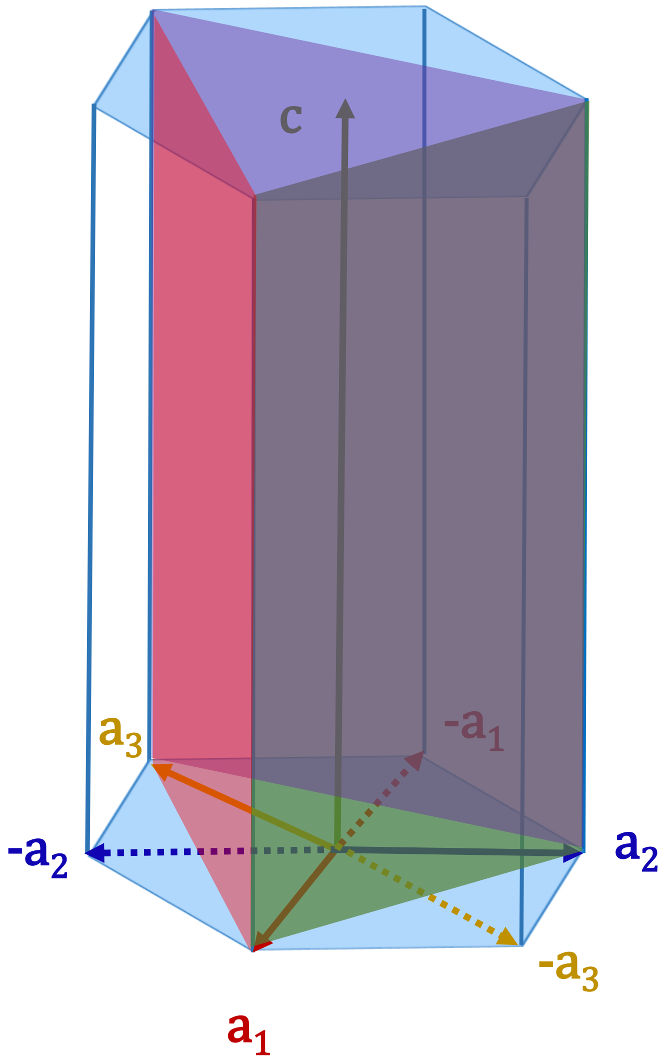
Prismatic planes : *Planes || to the c-axis*

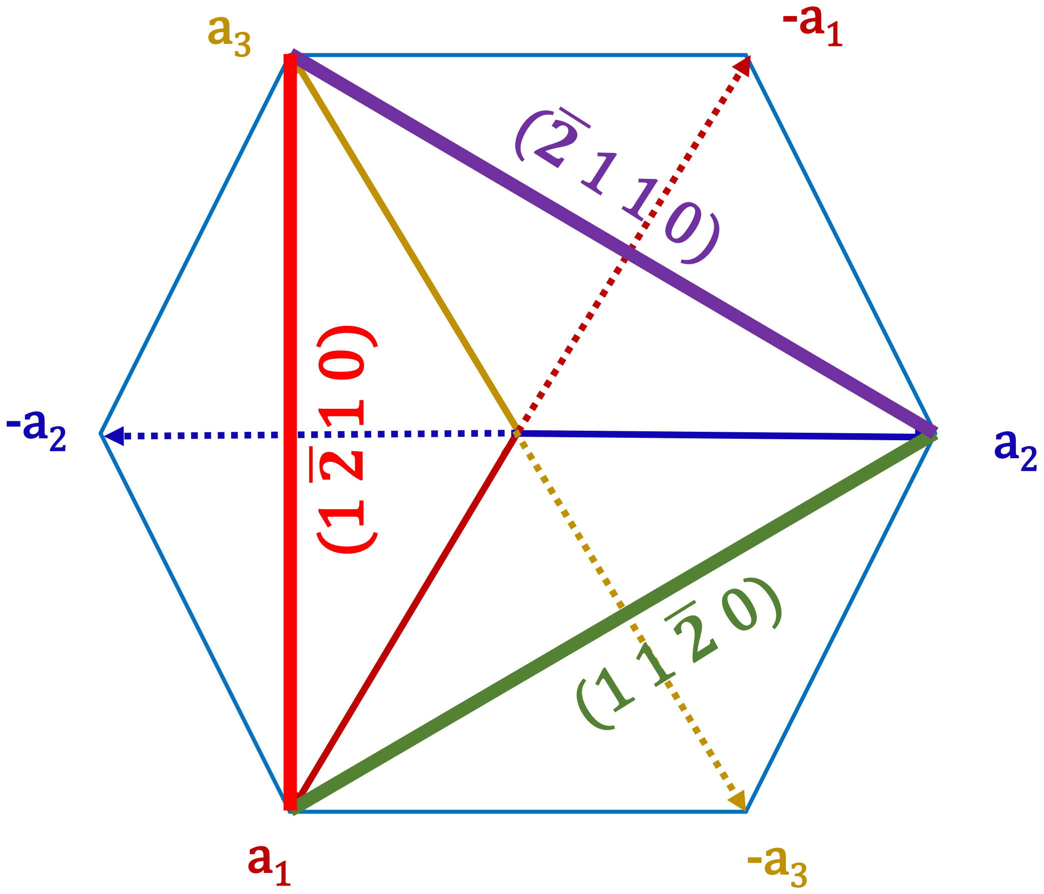


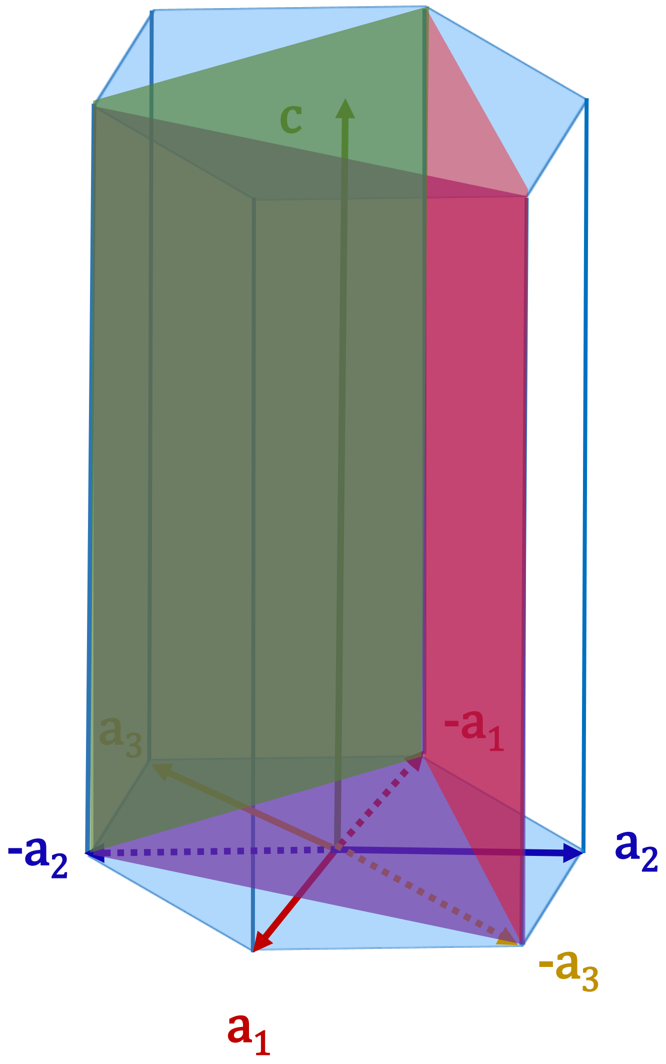


- The equivalent planes, (1 0 0), (0 1 0), $(1\ \bar{1}\ 0)$ defined by Miller indices, got transformed to $(1\ 0\ \bar{1}\ 0)$, $(0\ 1\ \bar{1}\ 0)$ and $(1\ \bar{1}\ 0\ 0)$ defined by Miller-Bravais indices.
- These have the same set of indices, and belong to the same family of planes: $\{1\ \bar{1}\ 0\ 0\}$

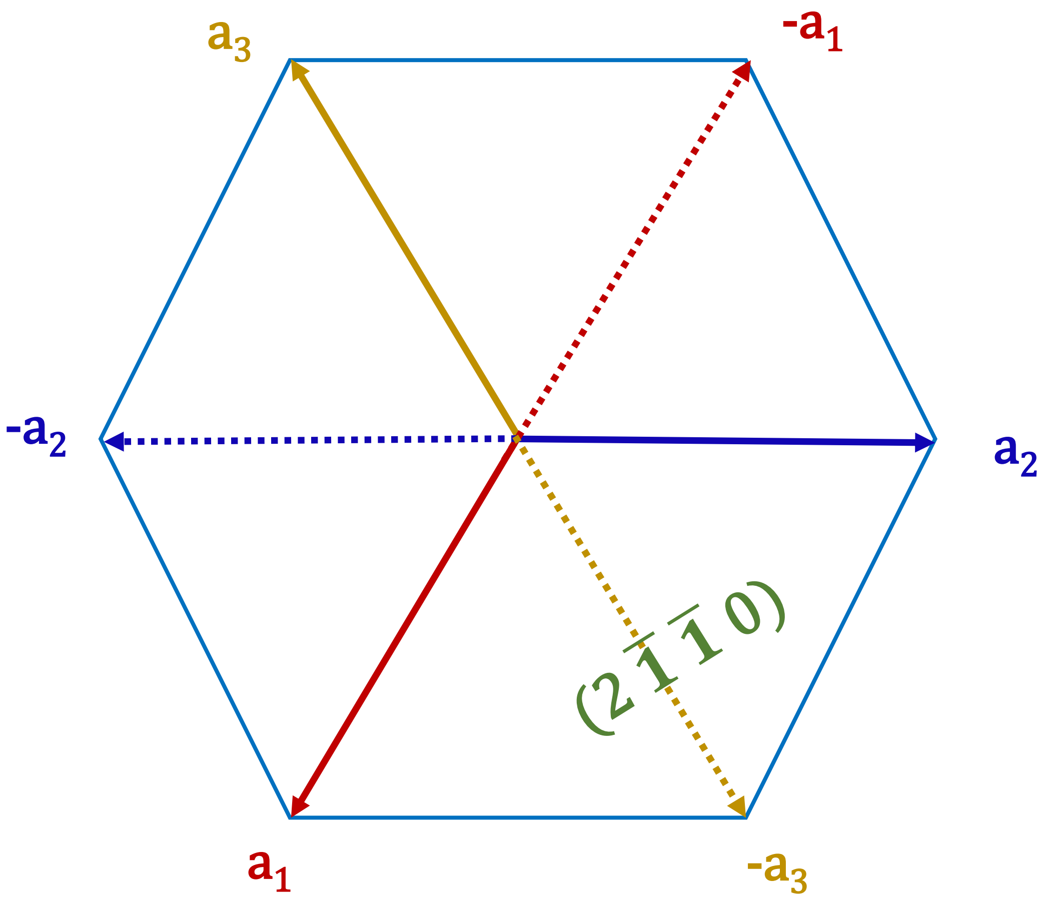
Prismatic planes : *Planes || to the c-axis*





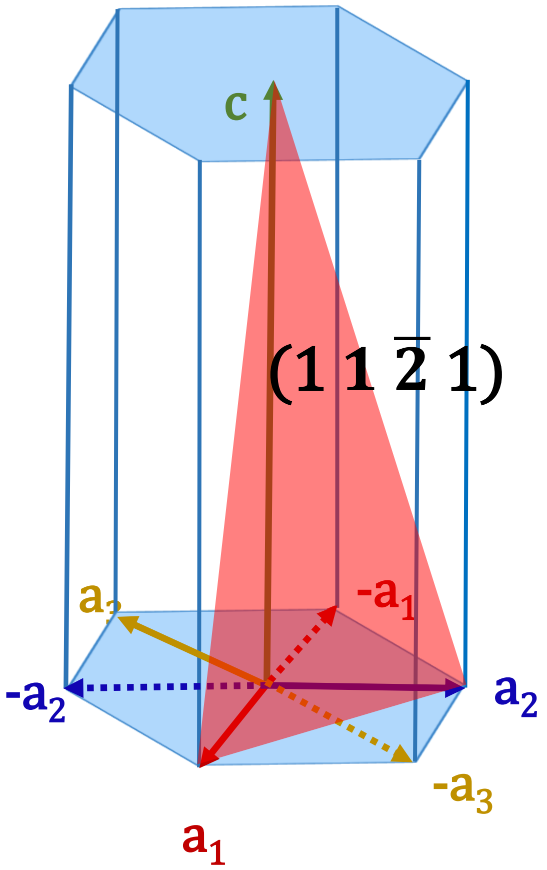


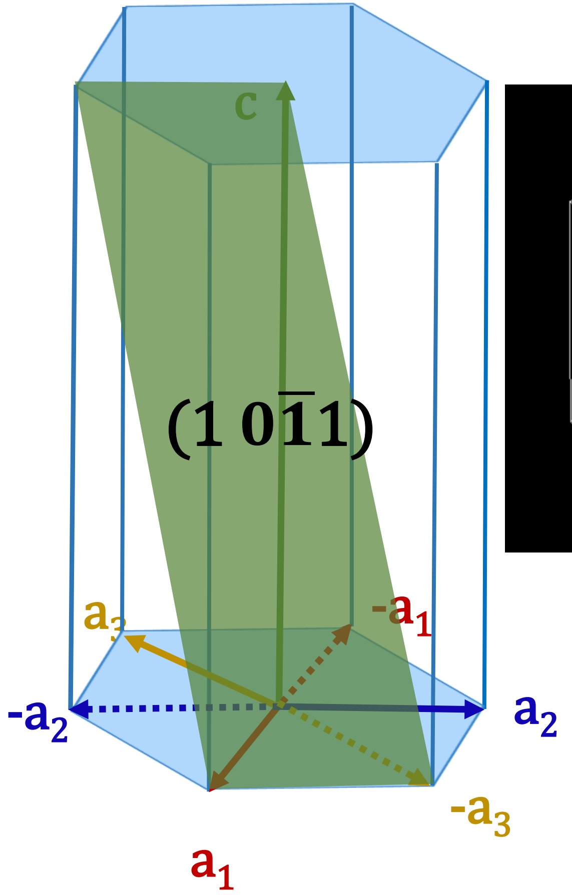
c
a_3
$-a_1$
$-a_2$
a_2
$-a_3$
a_1

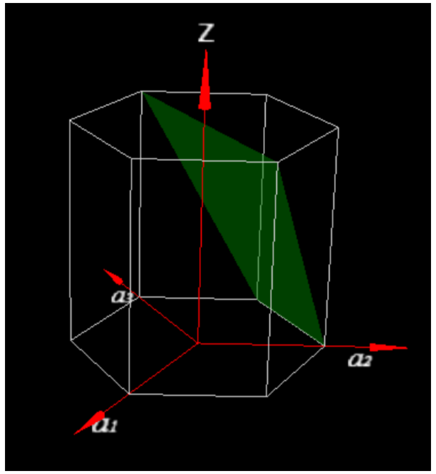


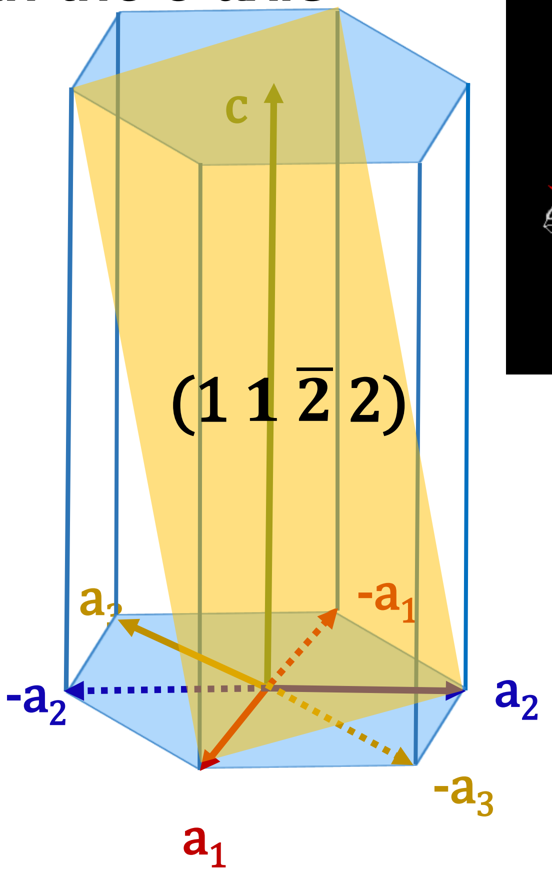
a_3
$-a_1$
$-a_2$
a_2
$(2\bar{1}\bar{1}0)$
a_1
$-a_3$

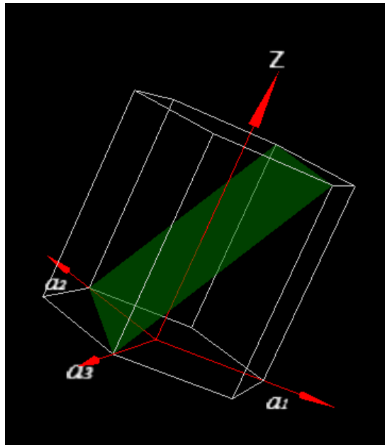
Pyramidal planes : *Planes which have finite intercepts with the c-axis*









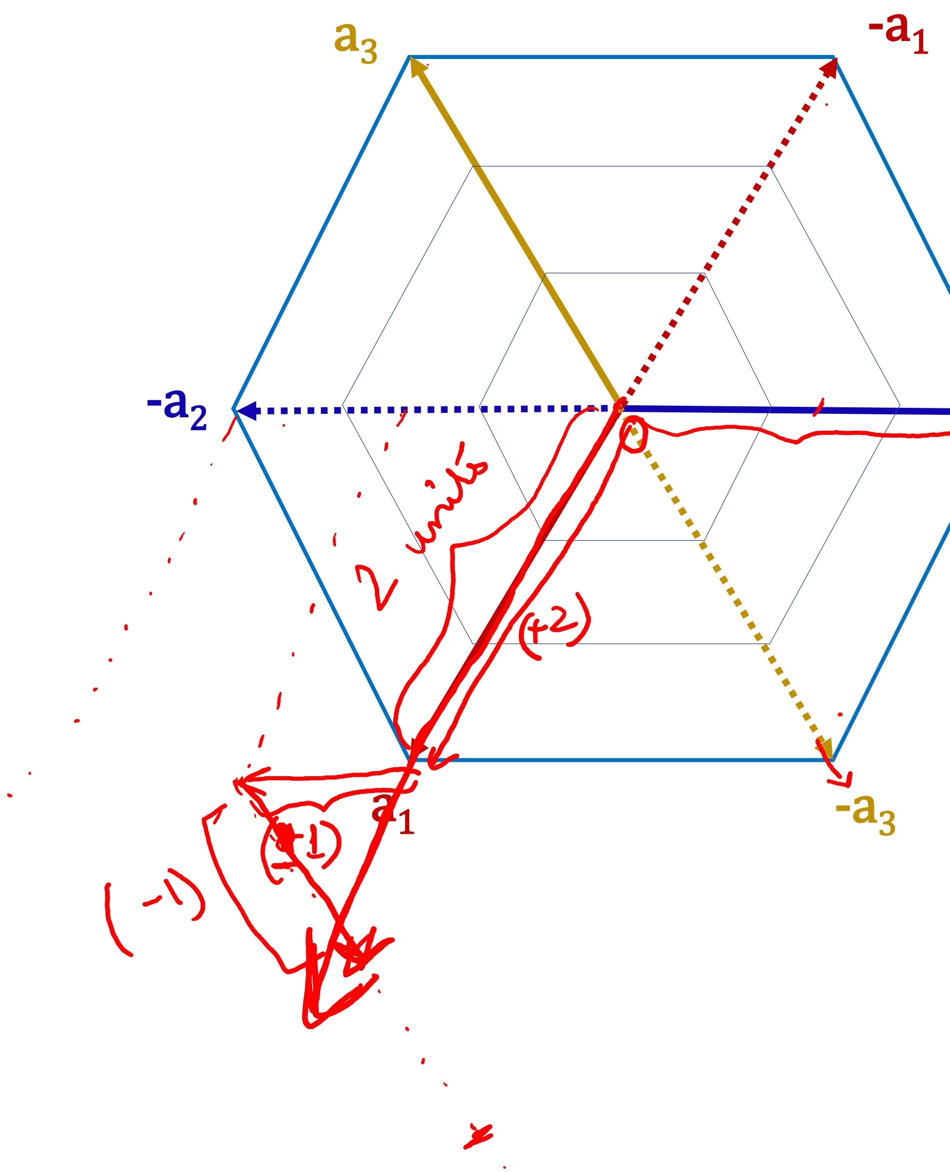


Miller-Bravais directions: *Axis directions*

$a_1 \Rightarrow [1\,0\,0\,0]$ ✗

a_1

$2\,\bar{1}\,\bar{1}\,0$



Highest integer $\Rightarrow 2$

(i) $a_1 \rightarrow (+2)$ units

$\Downarrow$

$a_2 \rightarrow (-1)$ units

$\Downarrow$

(f) $a_3 \rightarrow (-1)$ units

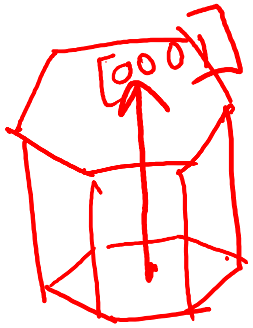
Miller-Bravais directions: *Axis directions*

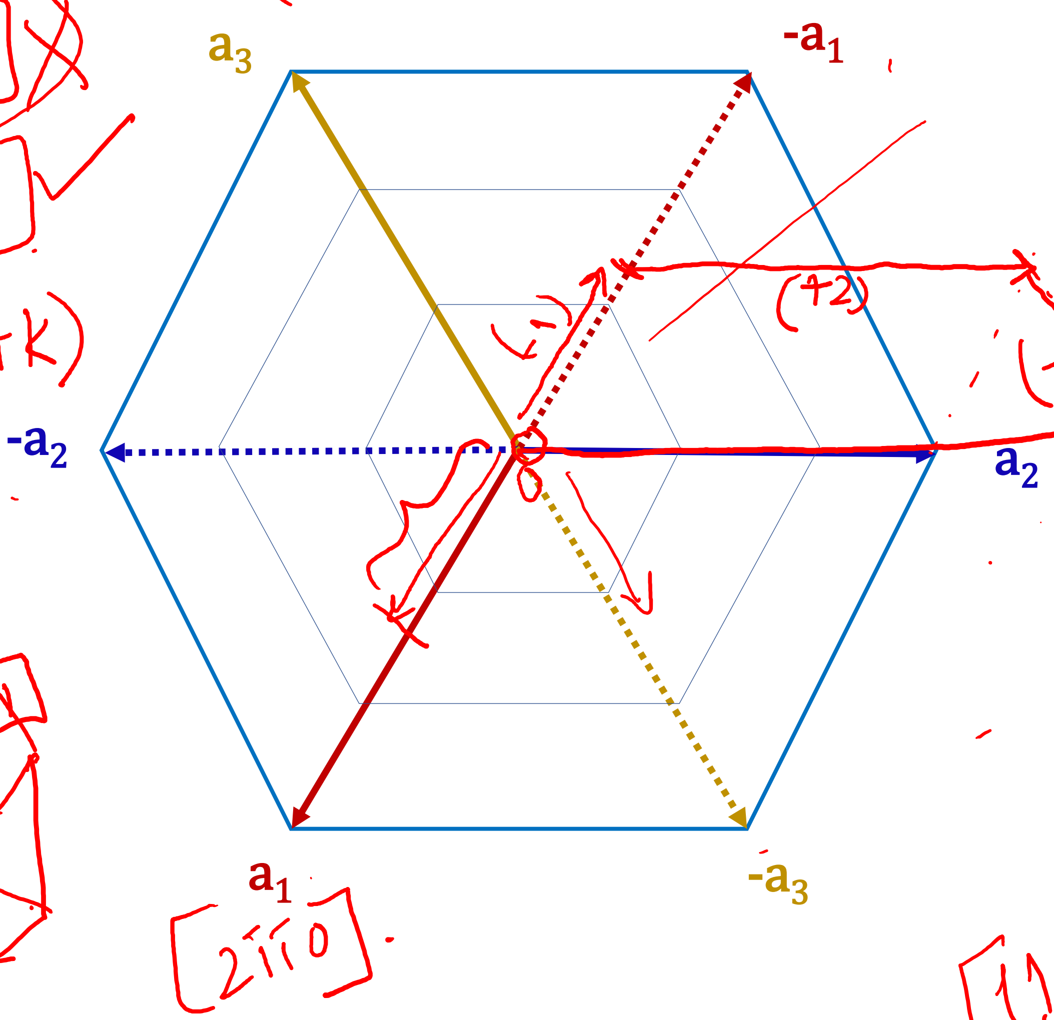
~~[1000]~~

[0001]

$i = -(h+k)$

c-axis





[$\bar{1}2\bar{1}0$]

a_1 (−1)

a_2 (+2)

a_3 (−1)

$2\,\bar{1}\,\bar{1}\,0$

$\bar{1}\,2\,\bar{1}\,0$

$\bar{1}\,\bar{1}\,2\,0$

$1\,1\,\bar{2}\,0$

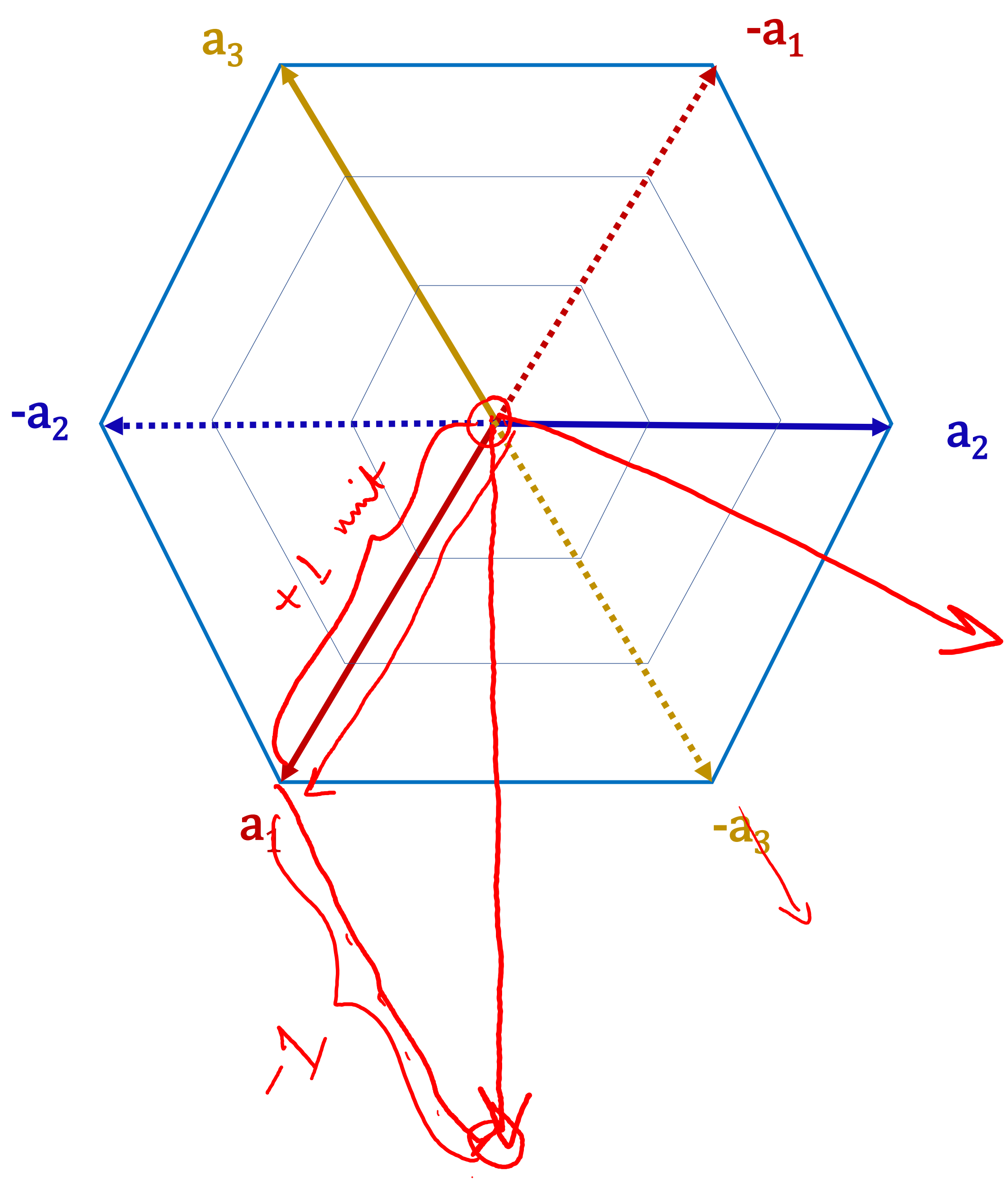
$\bar{2}\,1\,1\,0$

$1\,\bar{2}\,1\,0$

[0100]

- Basis vectors a_1, a_2 & a_3 are symmetrically related by a six-fold axis.
- The 3rd index is redundant and is included to bring out the equality between equivalent directions (like in the case of planes).

Miller-Bravais directions : *Diagonal directions*



$1\,0\,\bar{1}\,0$

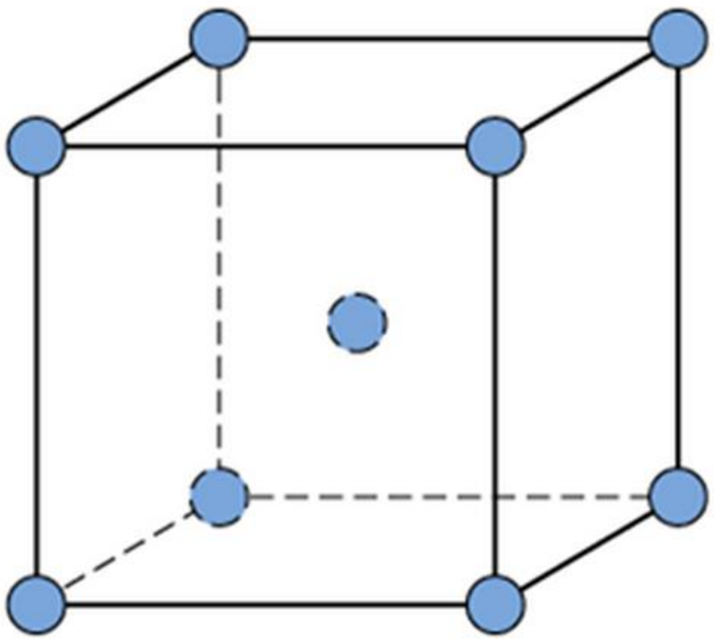
$0\,1\,\bar{1}\,0$

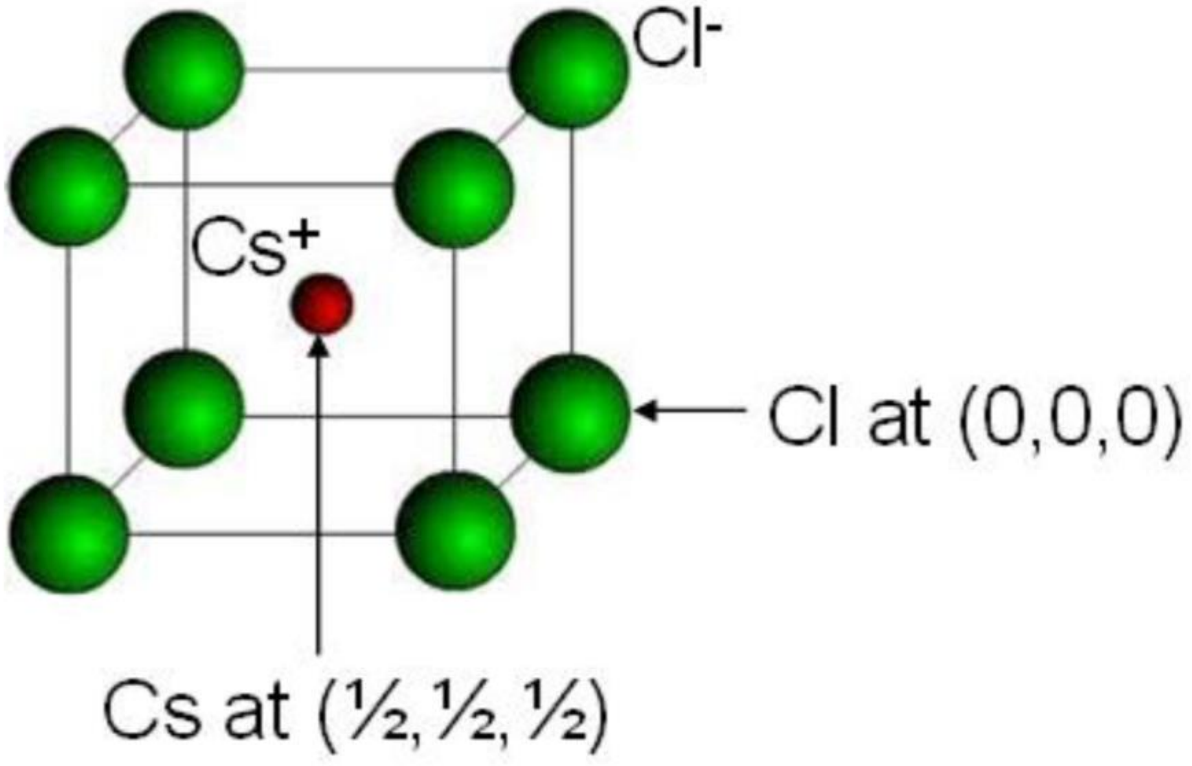
$\bar{1}\,1\,0\,0$

$\bar{1}\,0\,1\,0$

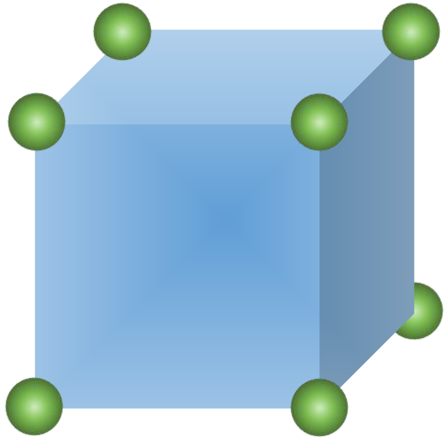
$0\,\bar{1}\,1\,0$

$1\,\bar{1}\,0\,0$

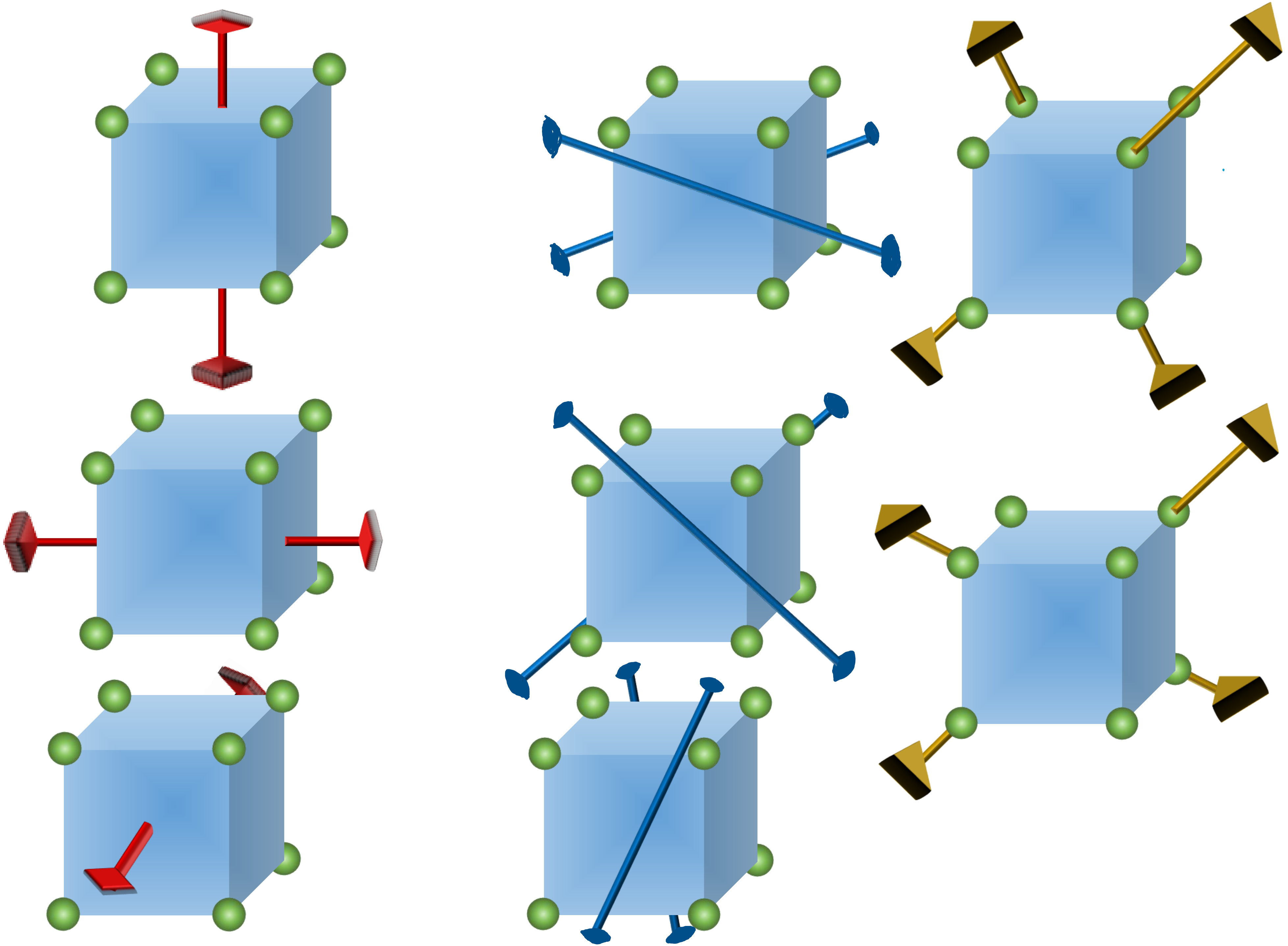




	Iron (Fe)	CsCl
Motif	1	2
Lattice type	Non-primitive	Primitive
Crystal system	Cubic	Cubic
Bravais lattice	Body centered cubic	Simple cubic



Point symmetry =1

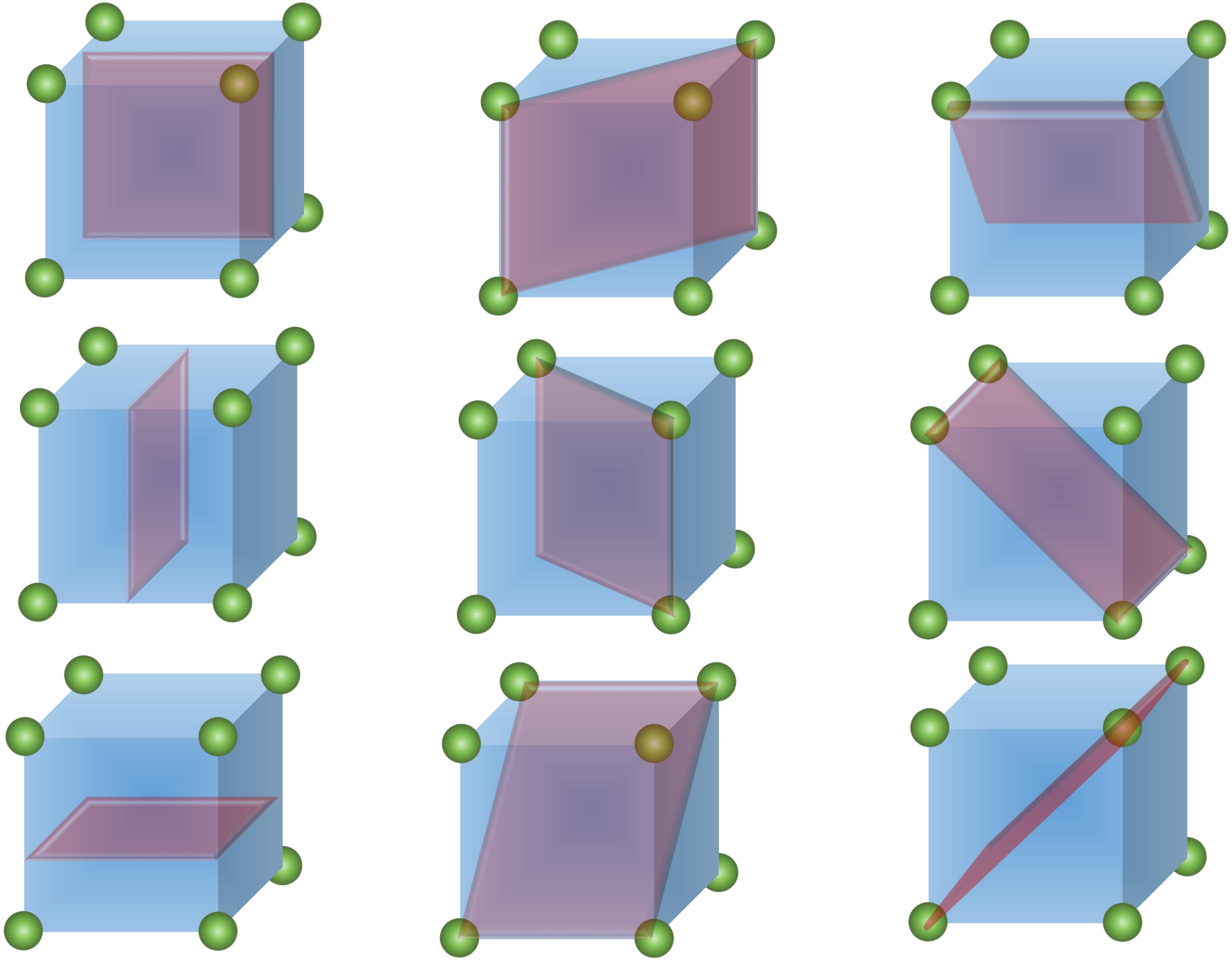


Line of symmetry:

4-fold: 3

2-fold: 6

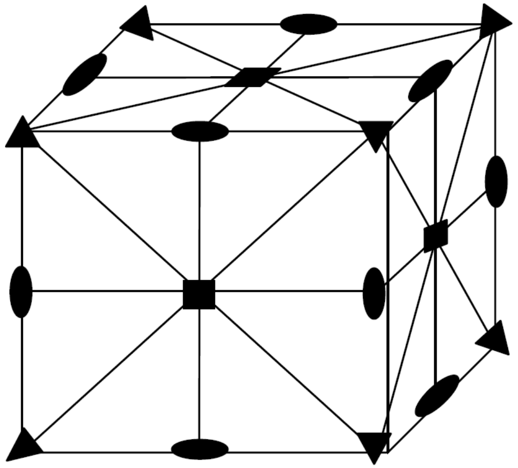
3-fold: 4



Plane of symmetry:

Mirror plane: 9

Total symmetry in a cube:
1 + 13 + 9 = 23



- What is the difference between crystal structure and crystal system?

- Do non-crystalline materials exhibit the allotropy/polymorphic phenomenon?

First QUIZ of MLL100

Date	: *January 25, 2022*
Day	: *Tuesday*
Time	: *10:30 a.m. – 10:50 a.m.*
Marks	: *10*
Mode	: *Online (Moodle)*
Syllabus	: *Topics covered until Jan 19, 2022*

MLL 100

Introduction to Materials Science and Engineering

Lecture-7 (January 18, 2022)

Dr. Sangeeta Santra (*ssantra@mse.iitd.ac.in*)

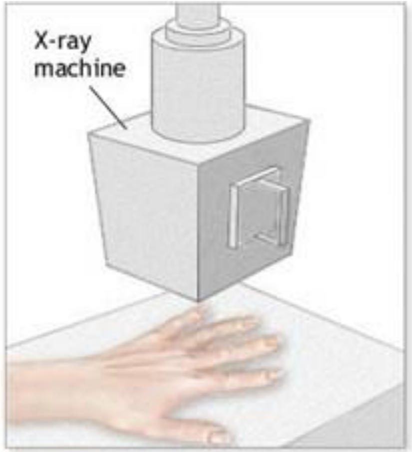
IIT Delhi
Department of Materials Science and Engineering

Topics covered

- Miller-Bravais indices of planes and directions in a hexagonal system


HAVE YOU SUFFERED A BROKEN BONE
IN A SLIP AND FALL?
Hupy and
Abraham s.c.
personal injury lawyers
hupy.com

X-ray diffraction



- ❑ Tool used to understand the crystallography of the material.
- ❑ Understanding of the basic principle involved with the technique (XRD).
- ❑ Case studies of XRD.

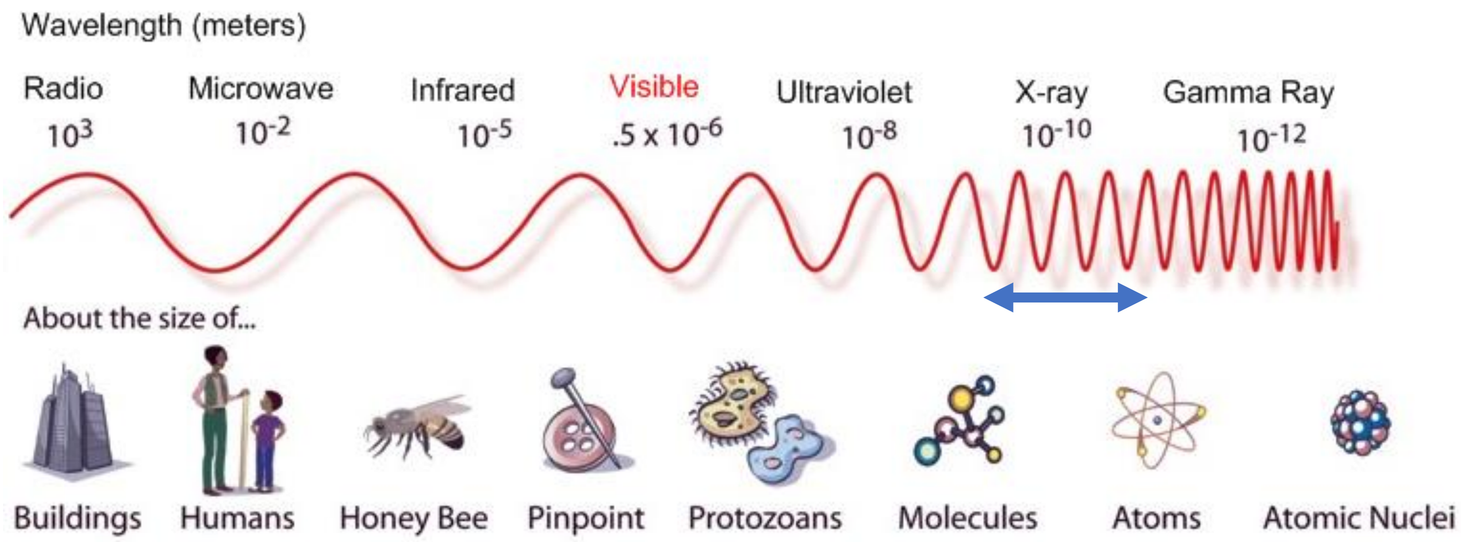
Why can X-ray be used for diffraction?

- X-radiation ("X-rays") is electromagnetic radiation with wavelengths between ~ 0.1Å and 100 Å, typically like the interatomic distances (~ 2-3 Å) in a crystal. It permits crystal structures to diffract X-rays.

Lattice parameter of Ni (a_{Ni}) = 3.52 Å

$\Rightarrow$ d_{hkl} is equal to a_{Ni} or less than that (e.g. $d_{111} = a_{Ni}/\sqrt{3} = 2.03$ Å)

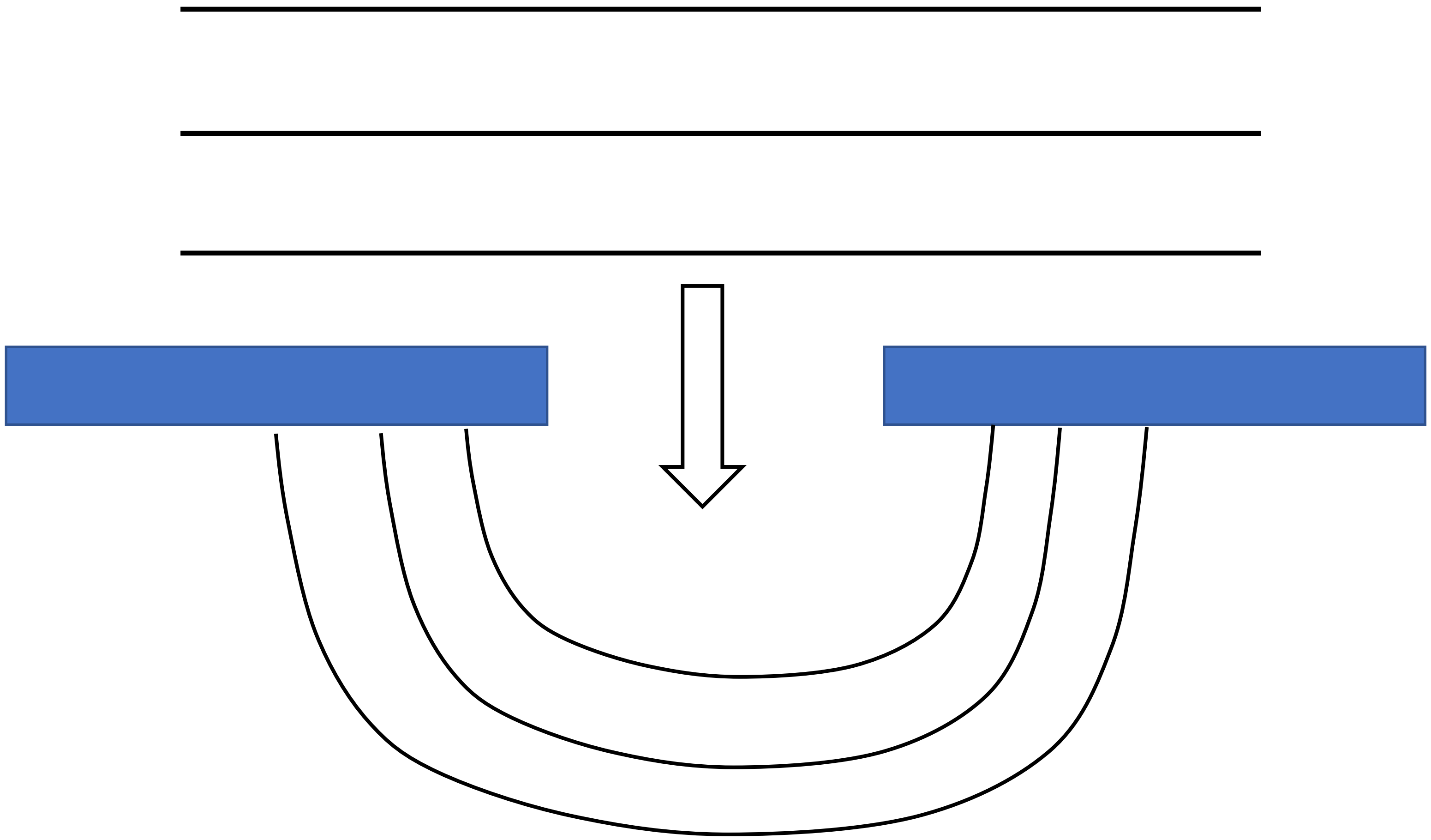
- Three possibilities (regimes) exist based on the wavelength (λ) and the spacing between the scatterers (a).
  - $\lambda < a \rightarrow$ transmission dominated.
  - $\lambda \sim a \rightarrow$ diffraction dominated.
  - $\lambda > a \rightarrow$ reflection dominated (surface phenomenon).



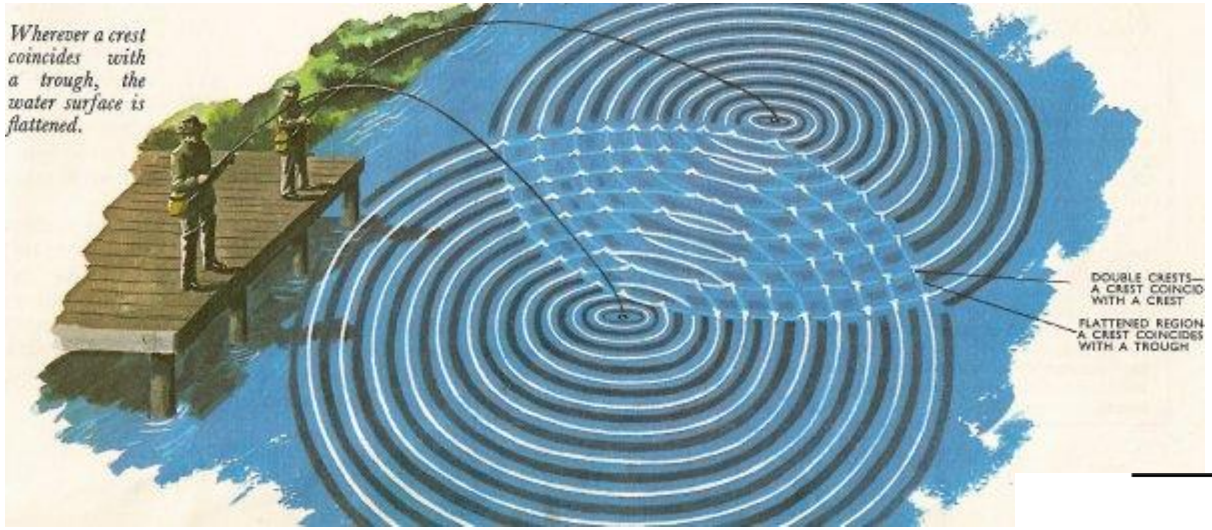
Electromagnetic Spectrum

Diffraction

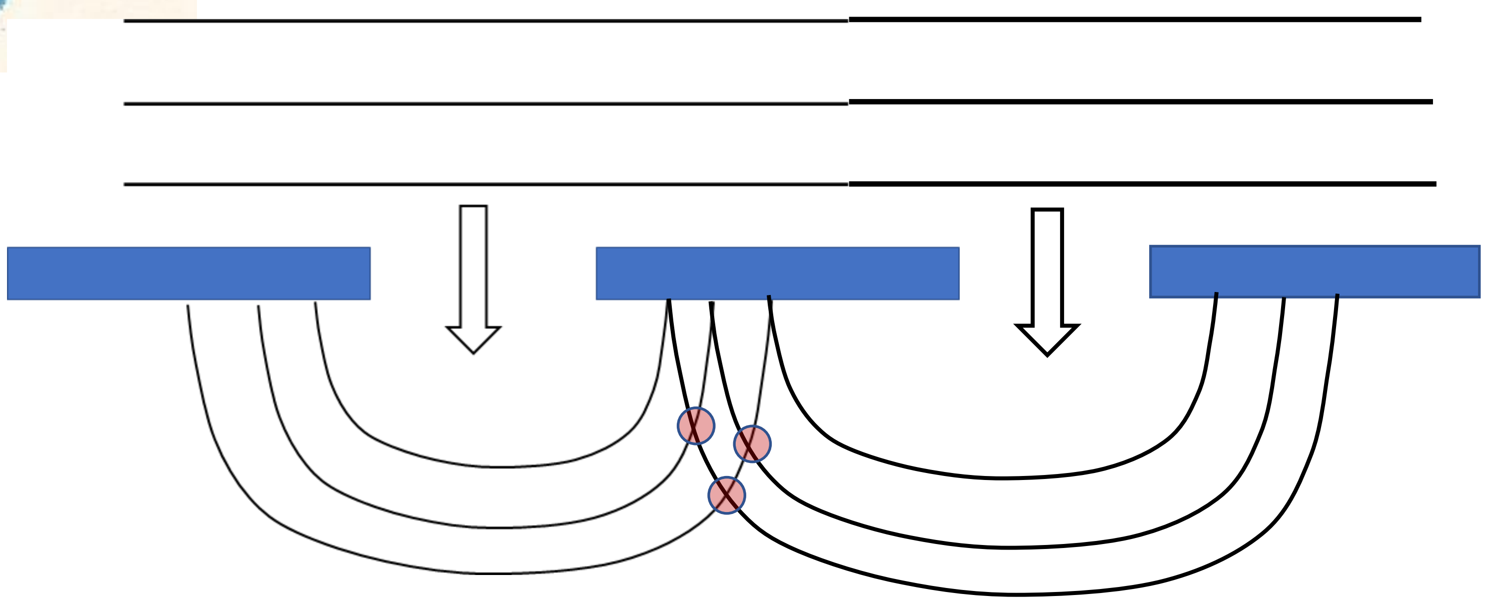
- Series of parallel waves passes through narrow spaces, get constricted, and either spreads out or bends.
- Series of narrowly spaces slits (diffraction grating) disperses parallel beams according to its wavelength.



Interference

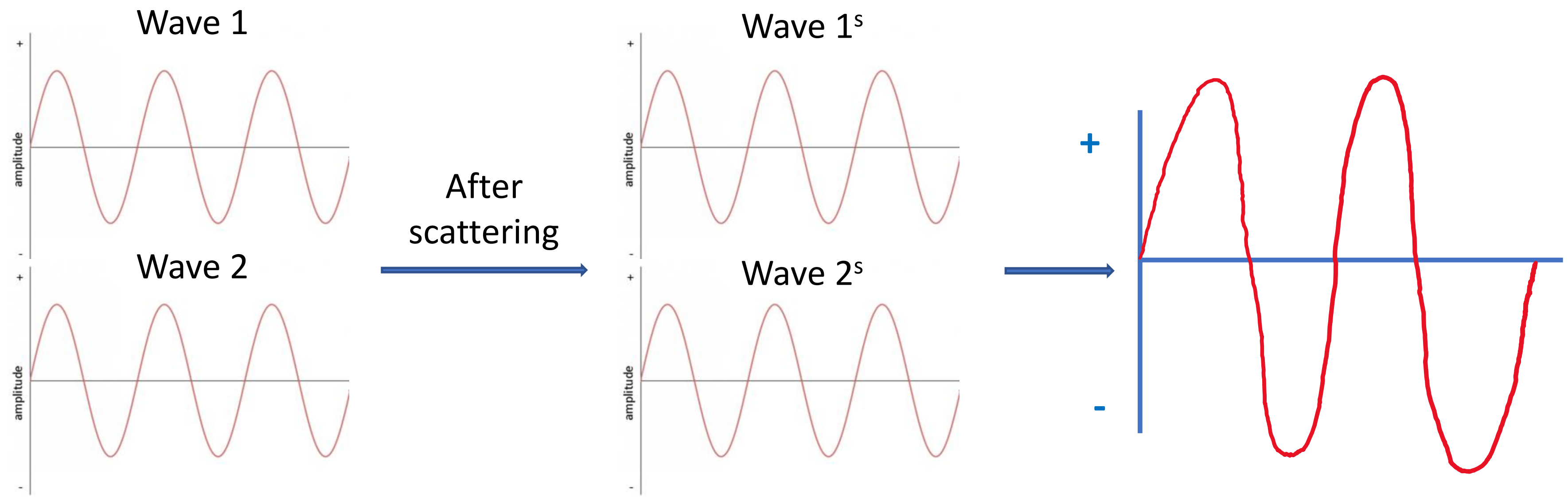


- Two waves encountering each other in the same medium, the effects can either be cancelled out or mutually reinforce each other.

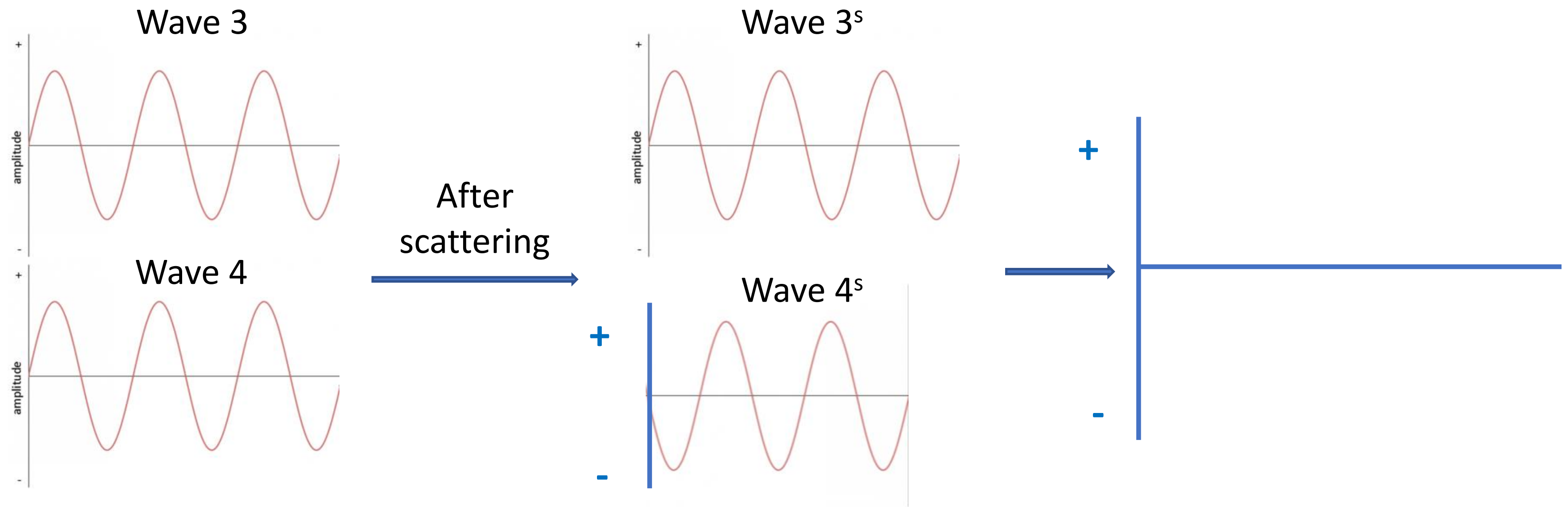


- Amplitude of the disturbance produced by the two combined waves = sum of individual disturbances.

Constructive and Destructive Interference

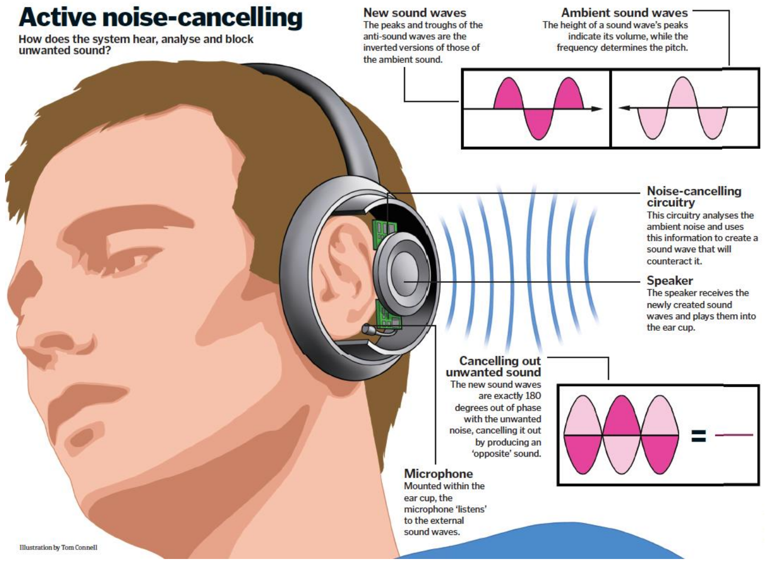


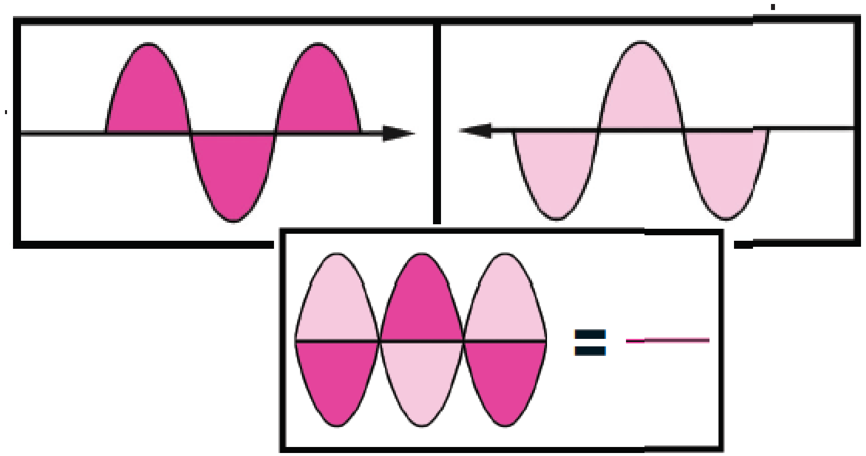
Waves that combine in phase -
---> **Constructive interference**
----> High intensity

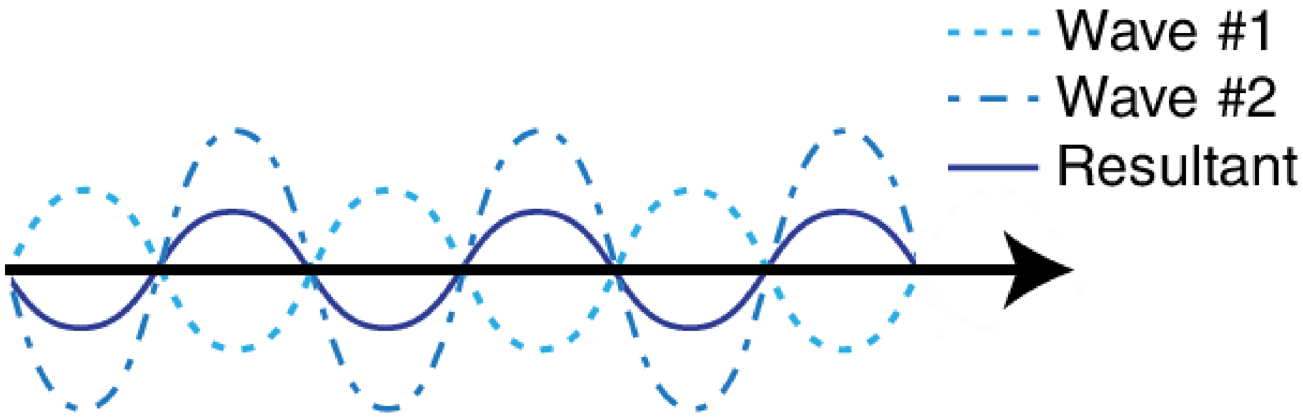


Waves that combine out-of-phase
---->**Destructive interference**
----> Zero intensity

Can something occur in between Constructive and Destructive Interference?

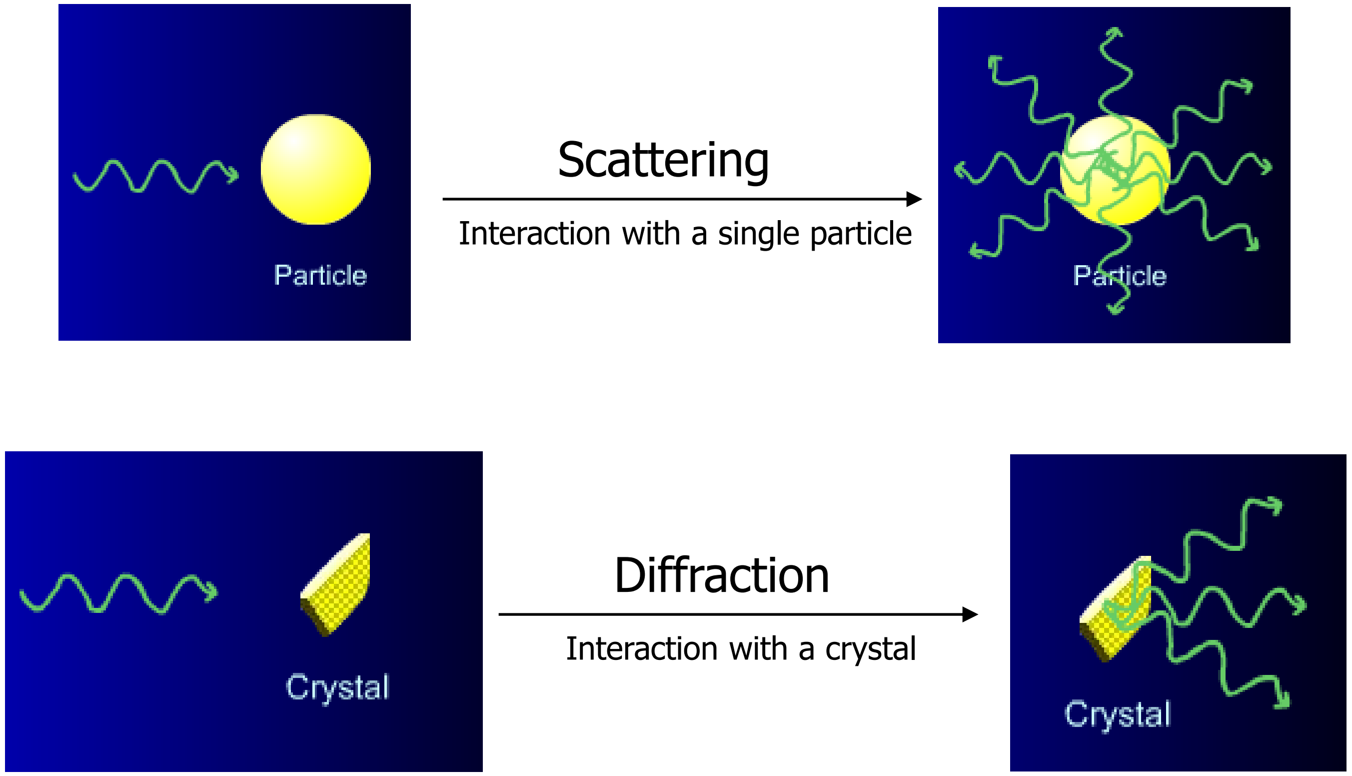






Diffraction in a crystal

A diffracted beam may be defined as a beam composed of many scattered rays mutually reinforcing each other

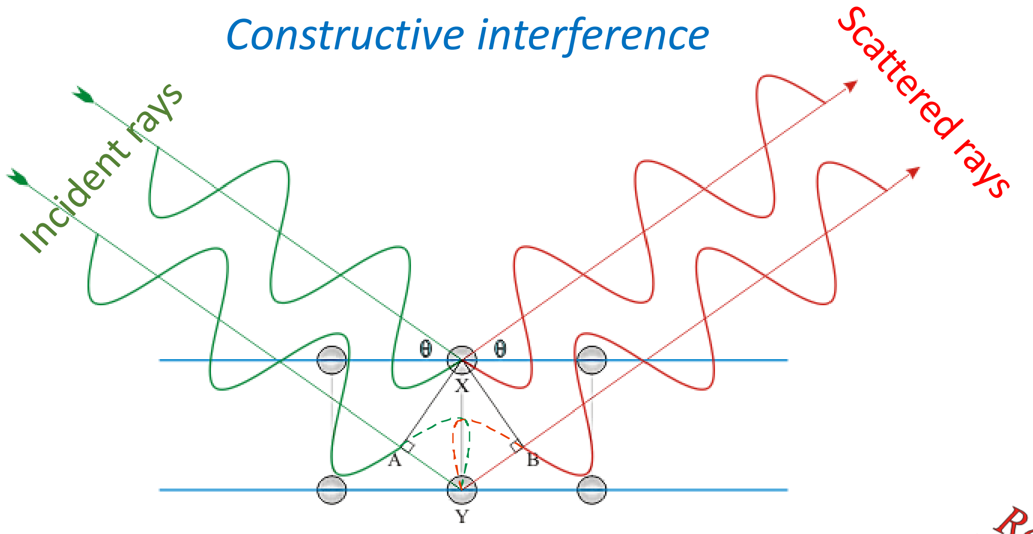


- ❑ **Random arrangement of atoms** in space gives rise to scattering in all directions: weak effect and intensities add.

- ❑ By **atoms arranged periodically** in space
    - ❑ In a few specific directions satisfying Bragg’s law: strong intensities of the scattered beam :Diffraction
    - ❑ No scattering along directions not satisfying Bragg’s law

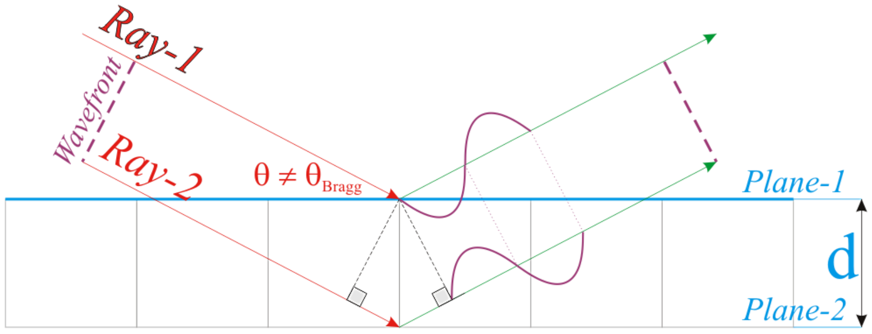
Consider waves scattered from two successive planes interfering constructively

Constructive interference

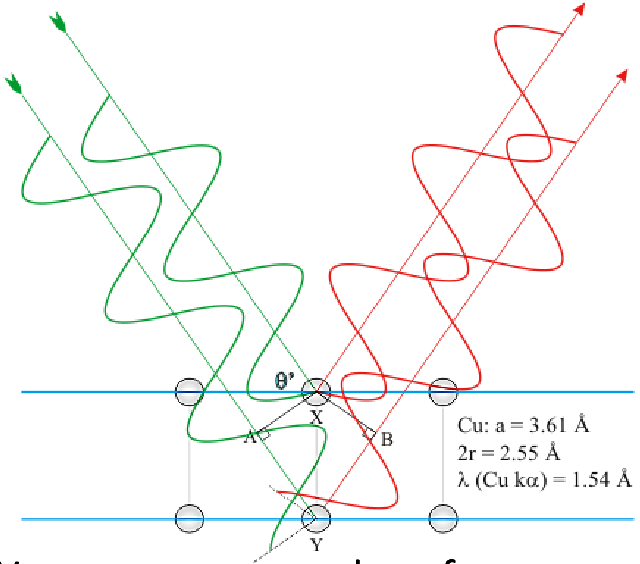


Phase difference of π introduced during the scattering by the atom.

Destructive interference



- Exact destructive interference (between two planes, with path difference of $\lambda/2$).
- The angle is not Bragg's angle.

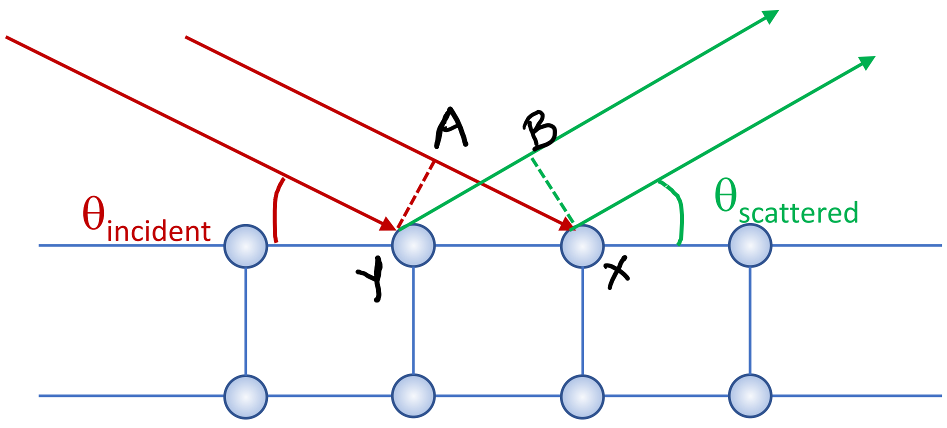


Waves scattered from two successive planes interfere (nearly) destructively at a different angle θ'

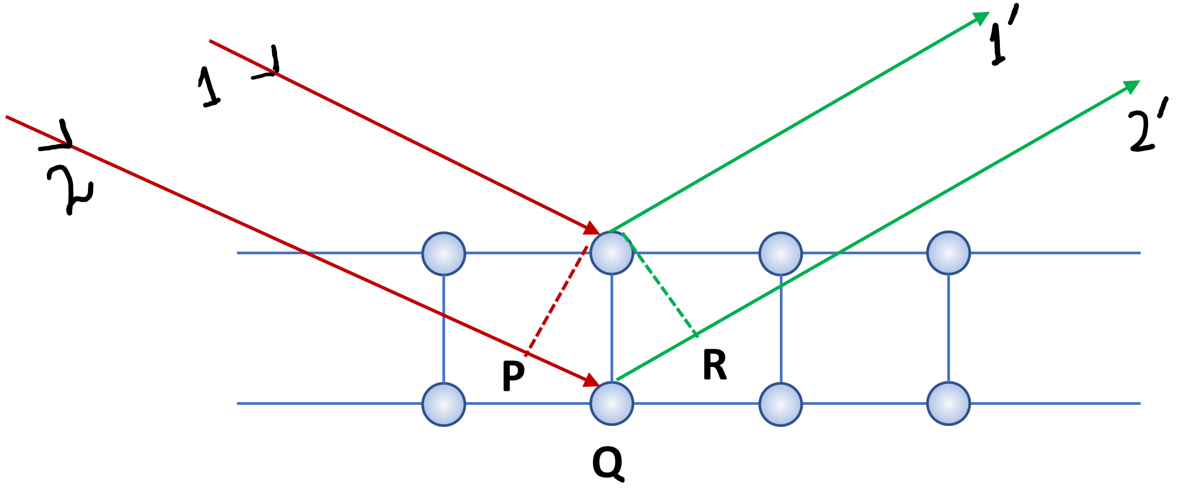
Consider a coherent wave of X-rays impinging on a crystal with atomic planes at an angle θ to the rays.

Incident and scattered waves are in phase if the:

In-plane scattering is in phase



Scattering from across the planes is in phase



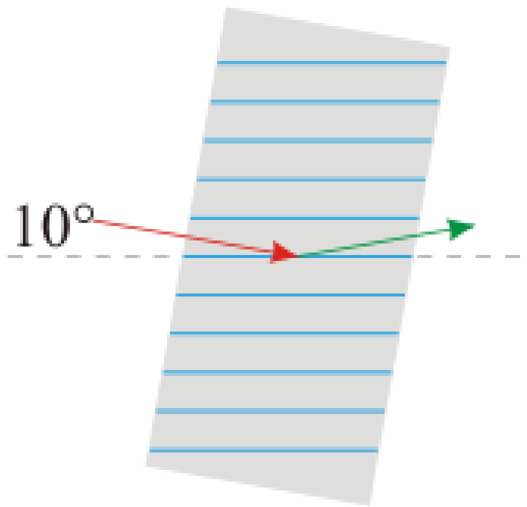
Extra path traveled by incident rays $\rightarrow$ AX

Extra path traveled by scattered rays $\rightarrow$ BY

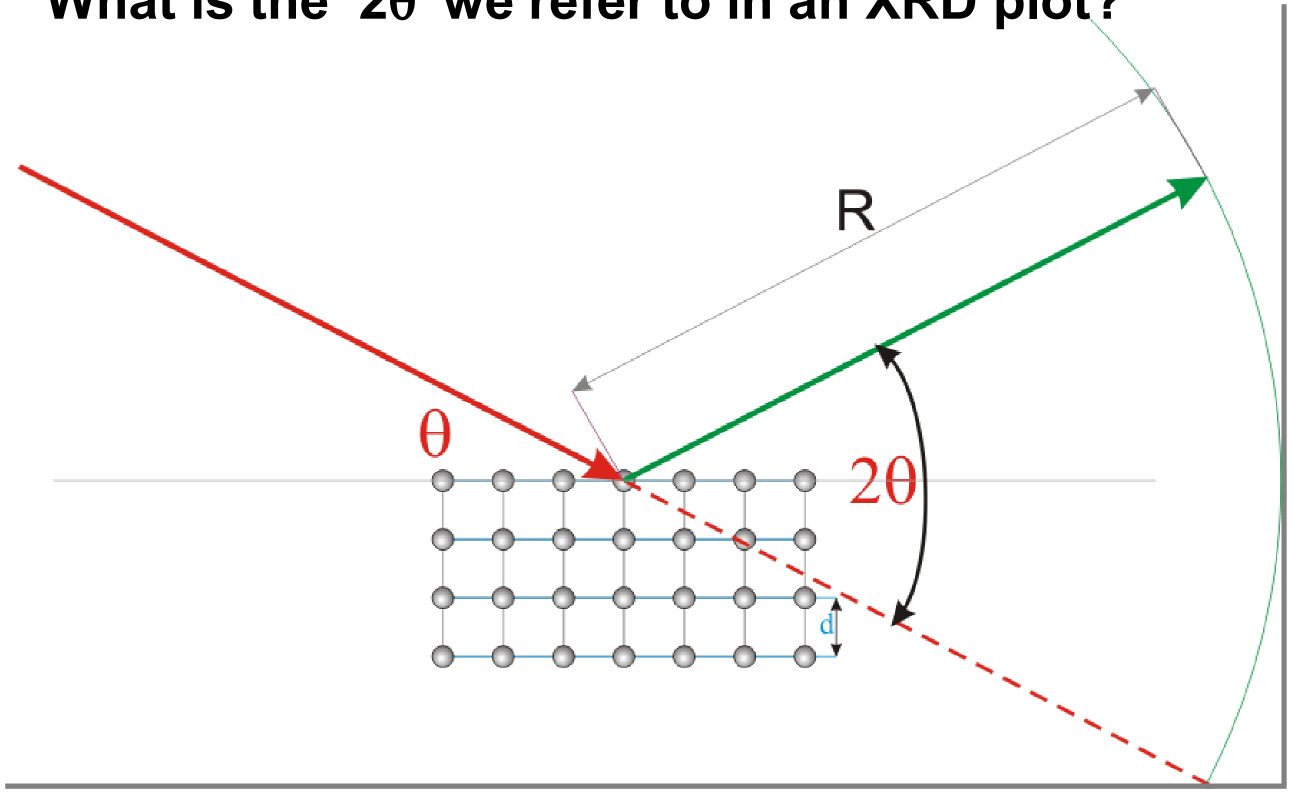
These can be in phase if $\rightarrow \theta_{incident} = \theta_{scattered}$

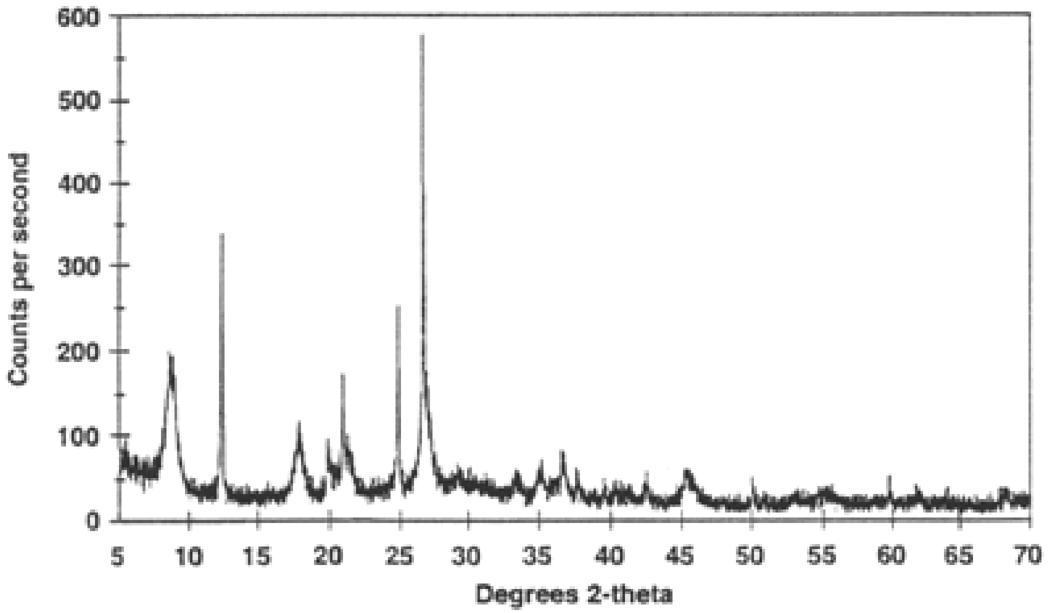
- The scattering planes have an interplanar spacing = ‘d’.
- Ray-2 travels an extra path as compared to Ray-1 (= PQR).
- Path difference between *Ray-1* and *Ray-2* = PQR = (d Sinθ + d Sinθ) = (2d.Sinθ).
- For constructive interference, this path difference should be an integral multiple of λ: $n\lambda$ = 2d Sinθ $\rightarrow$ the ***Bragg’s equation***

θ is the angle between the incident x-rays and the set of parallel atomic planes (which have a spacing d_{hkl}).

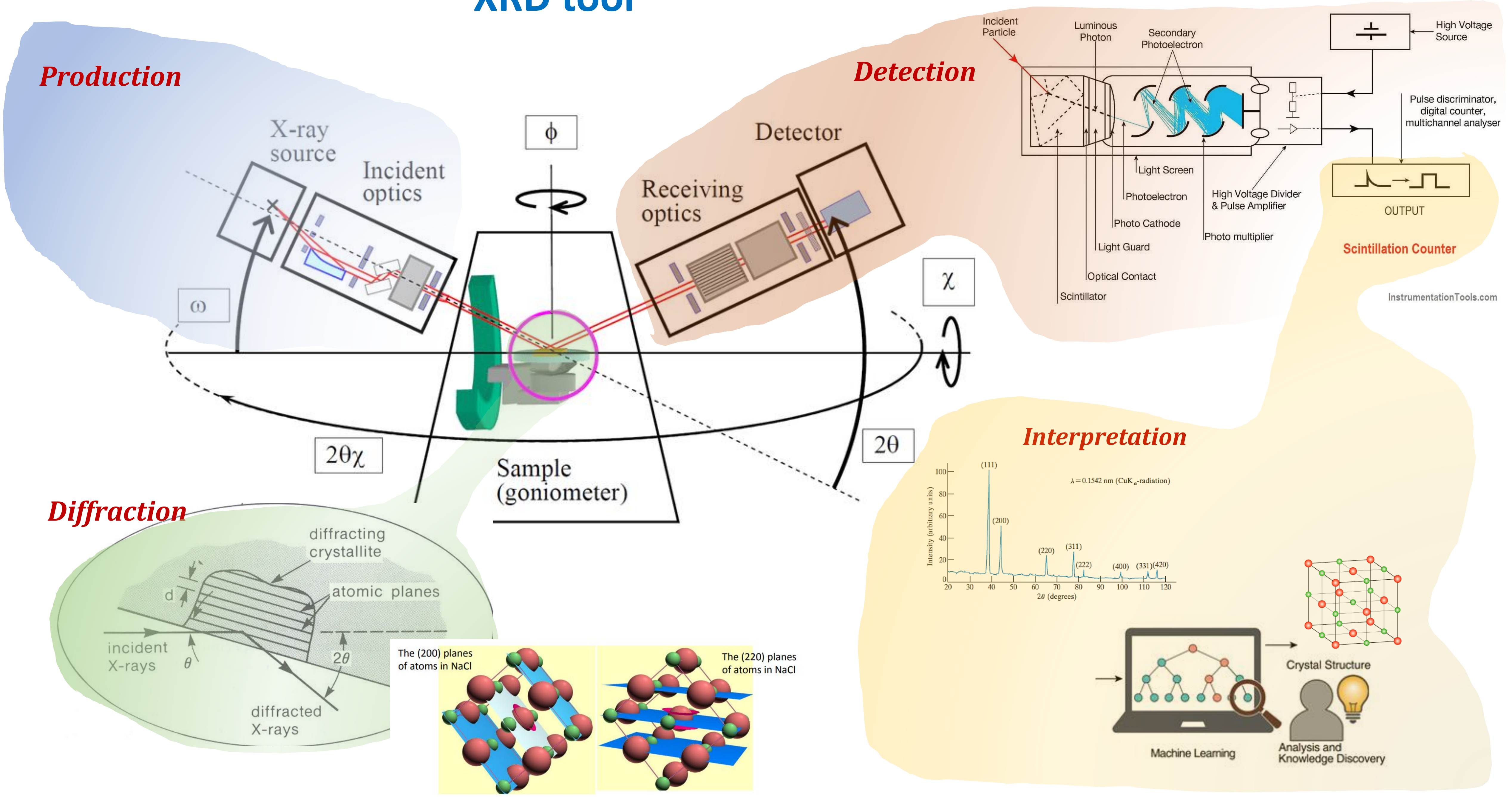


What is the '2θ' we refer to in an XRD plot?





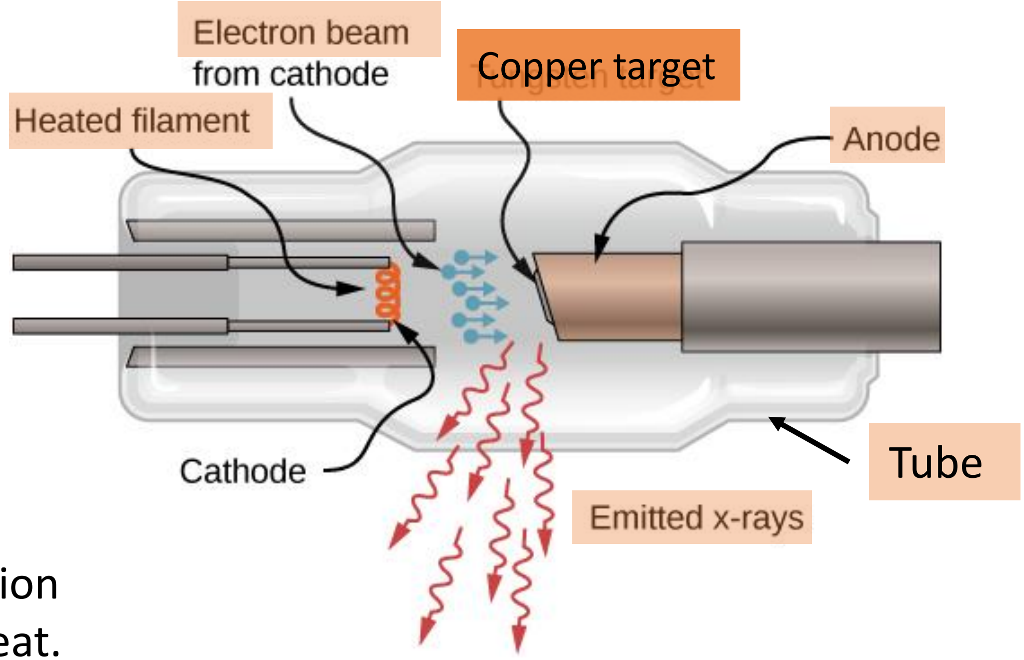
XRD tool


Production
X-ray source
Incident optics
ω
ϕ
Detector
Receiving optics
χ
2θχ
2θ
Sample (goniometer)
Detection
Incident Particle
Luminous Photon
Secondary Photoelectron
High Voltage Source
Pulse discriminator, digital counter, multichannel analyser
Light Screen
Photoelectron
High Voltage Divider & Pulse Amplifier
Photo Cathode
Photo multiplier
Light Guard
Optical Contact
Scintillator
OUTPUT
Scintillation Counter
InstrumentationTools.com
Diffraction
diffracting crystallite
atomic planes
d
incident X-rays
θ
2θ
diffracted X-rays
The (200) planes of atoms in NaCl
The (220) planes of atoms in NaCl
Interpretation
λ = 0.1542 nm (CuKα-radiation)
Intensity (arbitrary units)
2θ (degrees)
(111)
(200)
(220)
(311)
(222)
(400)
(331)
(420)
Crystal Structure
Machine Learning
Analysis and Knowledge Discovery

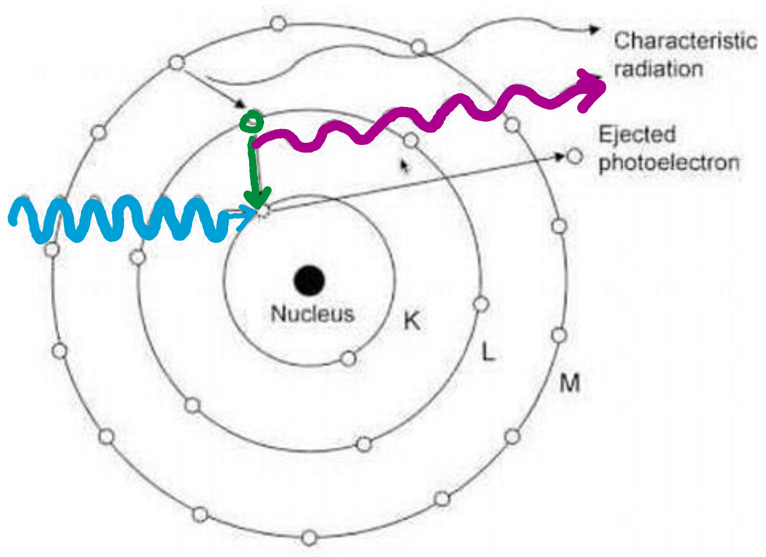
How are X-rays produced?

- *X-rays are produced when high-energy charged particles (electrons) accelerated through very high potential difference (30 kV) collide with matter.*

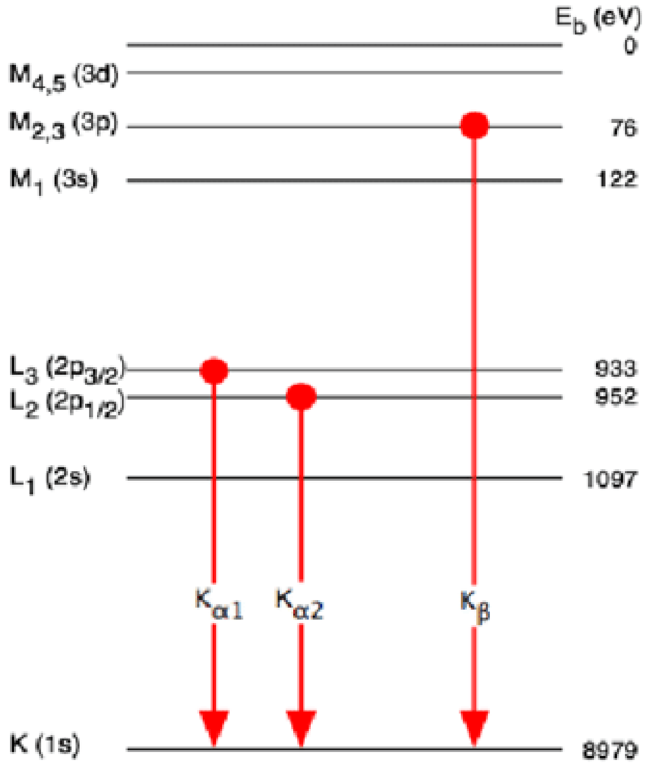
- Laboratory source of X-rays consists of an evacuated tube.
- Electrons are emitted from a heated tungsten filament.
- Electron beam accelerated towards an anode by an electric potential difference of ~ 30 kV to impinge on a water-cooled metal target.
- Electrons strike the Cu target fixed to the anode.
- A spectrum of X-rays get emitted.
- X-rays leave the tube through Be window.



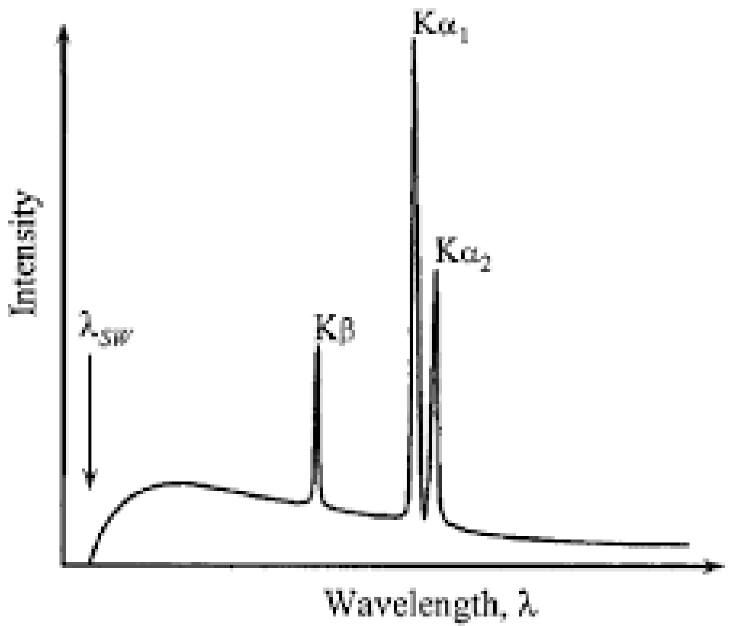
- Continuous cooling of anode is necessitated because only a small fraction of electron energy gets converted to X-ray and rest get converted to heat.



- Incident electrons with sufficient energy ionizes Cu 1s electron.
- An electron from outer orbital (2p or 3p) immediately drops down to the vacant K-level.
- Energy released in the transition appears as X-ray radiation.
- Transition energies have fixed values, so, a spectrum of characteristic X-rays results.
- Consider Cu, 2p ------> 1s transition ($\lambda_{K\alpha}$ = 1.5418 Å) and 3p -----> 1s transition ($\lambda_{K\beta}$ = 1.3922 Å) [K_α is more intense than K_β].



Characteristic X-ray: caused by electronic transitions within an atom



- K_α is a doublet (K_{α_1} = 1.54051 Å, K_{α_2} = 1.54433 Å)
- The 2p ---> 1s has a slightly different energy for the two possible spin states of the 2p electron which makes the transition, relative to the spin of the vacant 1s orbital.
- K_{α_1} and K_{α_2} are not sometimes resolved and appear as a single peak.

MLL 100

Introduction to Materials Science and Engineering

Lecture-8 (January 19, 2022)

Dr. Sangeeta Santra (*ssantra@mse.iitd.ac.in*)

IIT Delhi
Department of Materials Science and Engineering

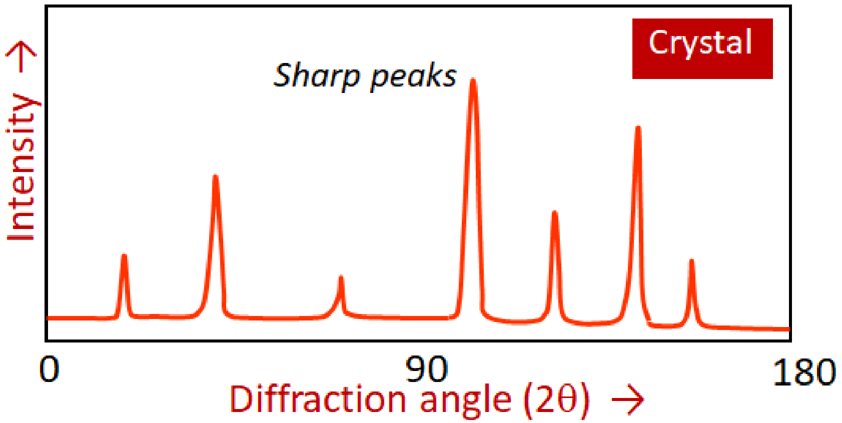
Topics covered

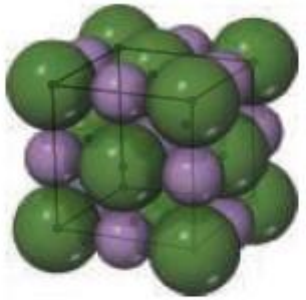
- X-ray diffraction

What is an XRD used for?

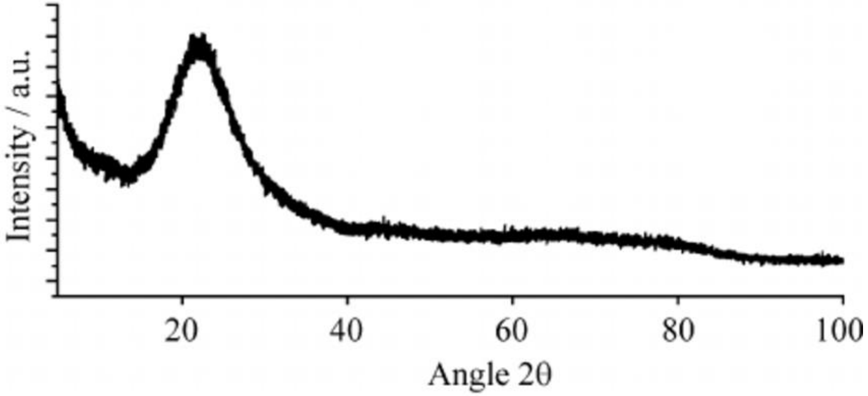
- Distinguishing between amorphous and crystalline solids

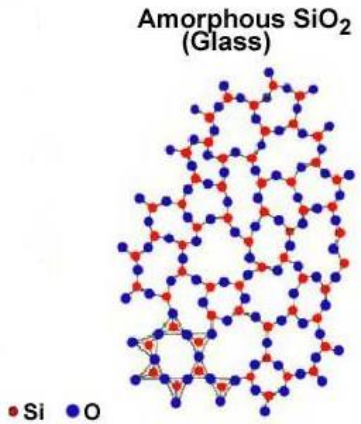
Crystalline



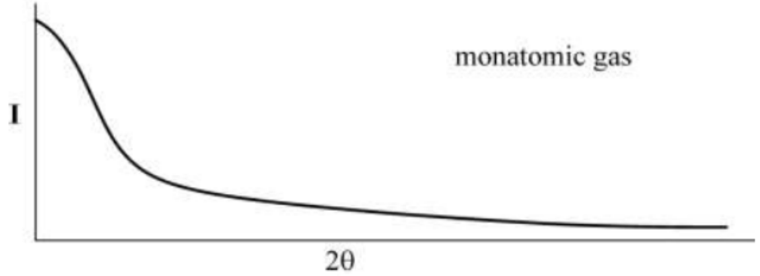


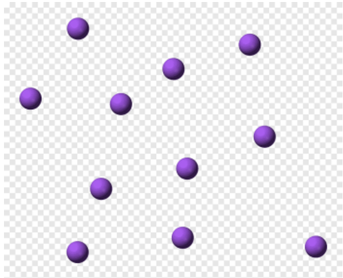
Amorphous





Monoatomic gas



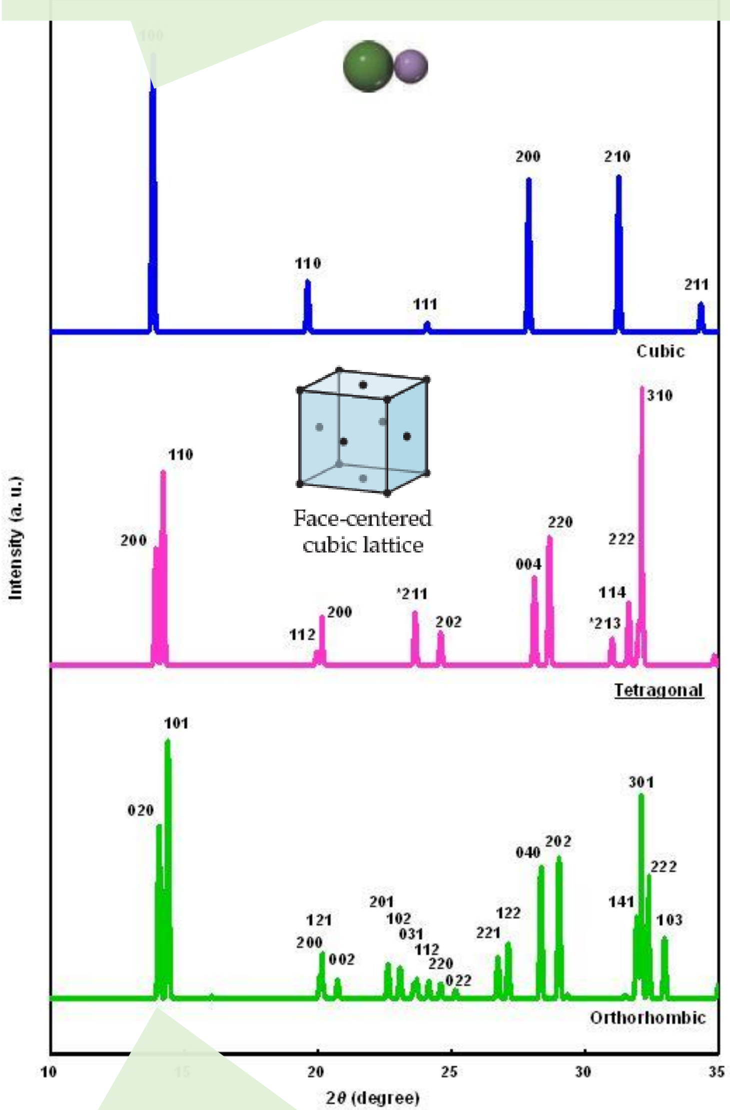


What is an XRD used for?

How does a crystal scatter these X-rays to give a diffraction pattern? → Bragg's equation

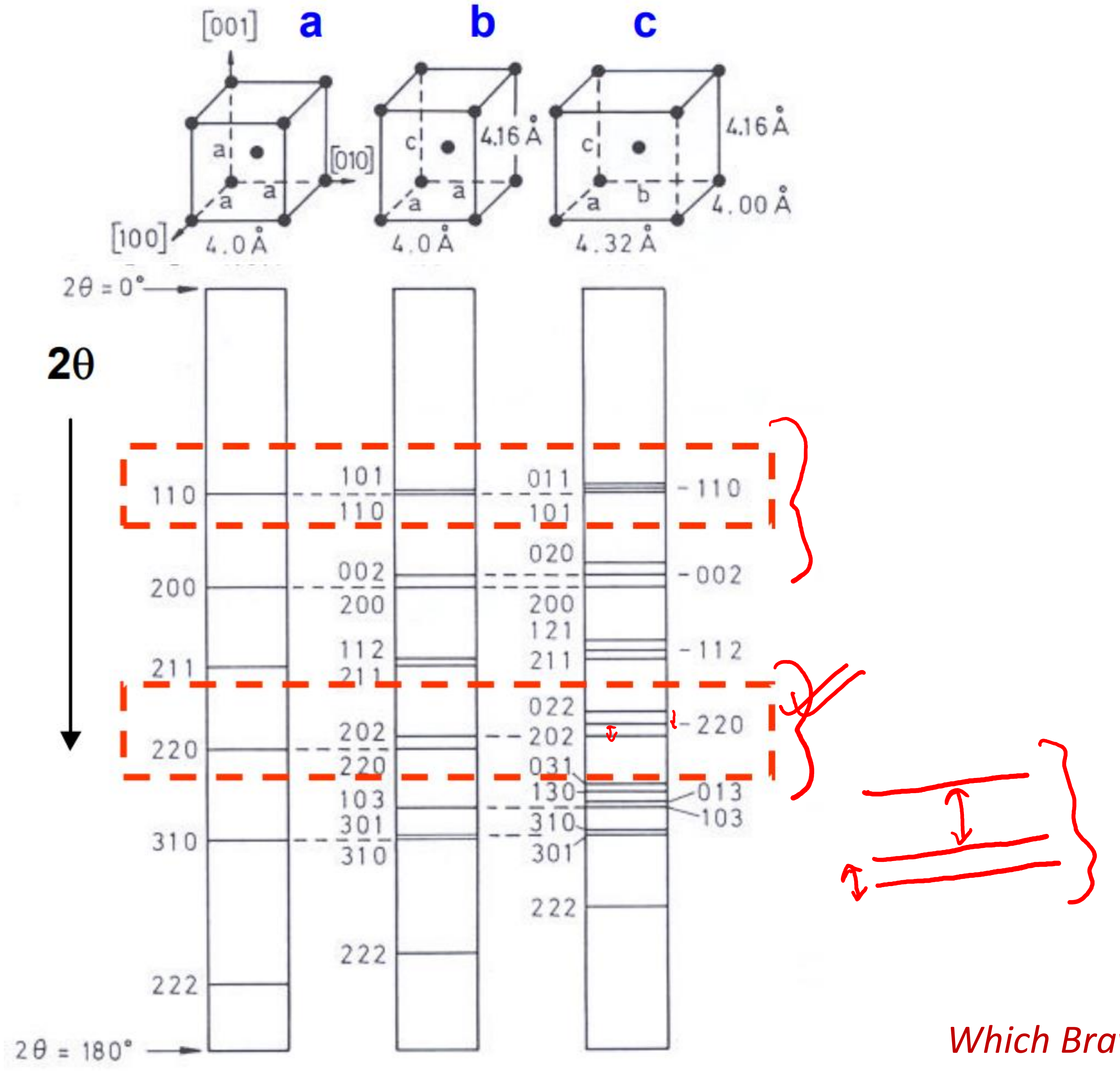
- ❑ Identification of crystalline materials
- ❑ Determination of the structure of crystalline solids
  - Determination of lattice parameter
  - Determination of Bravais lattice

What determines the intensity of the XRD peaks? → Motif (Many other factors also contribute to the intensity of a given peak)



What determines the position of the XRD peaks? → Characteristics of lattice.

Phase identification



What is the symmetry on XRD pattern?

- Cubic
  Lattice parameter = a (a = b = c)

- Tetragonal
  Lattice parameter: a and c (a = b ≠ c)

- Orthorhombic
  Lattice parameter: a, b, c (a ≠ b ≠ c)

202
$20\bar{2}$

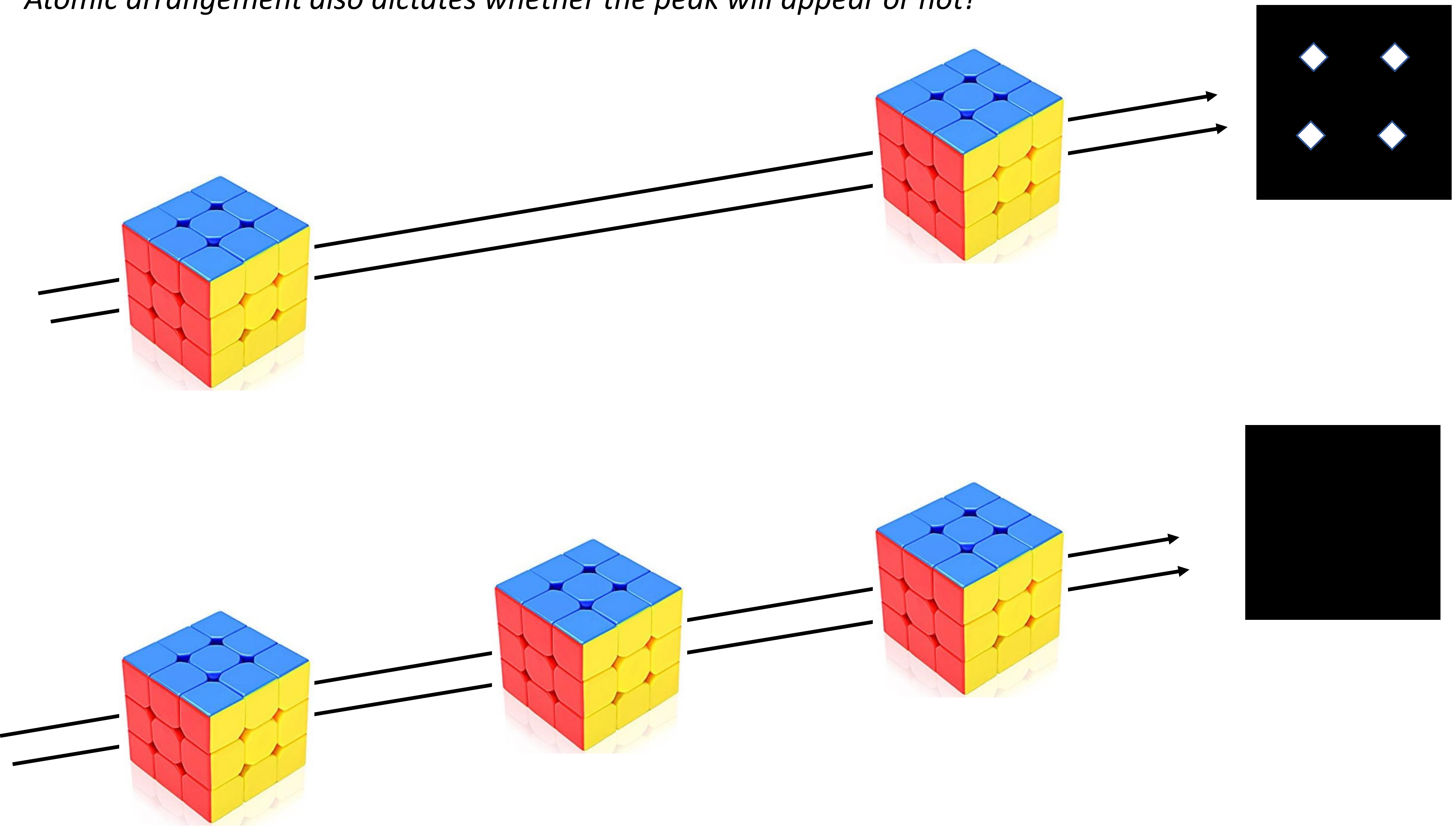
Triclinic
$\alpha \neq \beta \neq \gamma \neq 90$
$a \neq b \neq c$

- Number of peaks
- Peak position
- Peak splitting

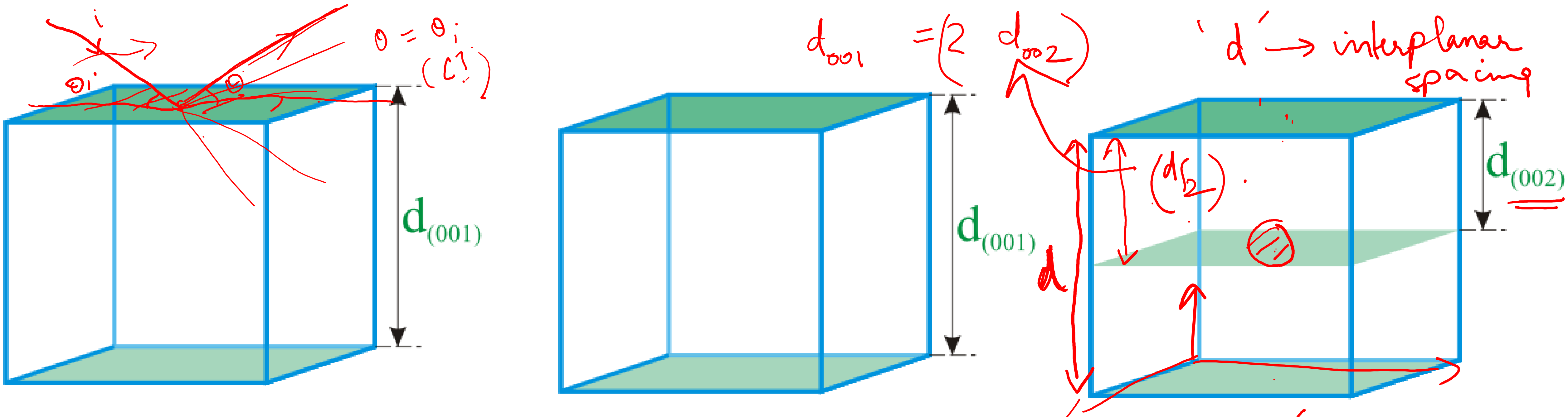
{220} (202) (220) (022)

Which Bravais lattice may produce the first XRD peaks?

Atomic arrangement also dictates whether the peak will appear or not!



Systematic absence



$\theta = \theta_i$

$d_{001} = 2\, d_{002}$

'd' → interplanar spacing

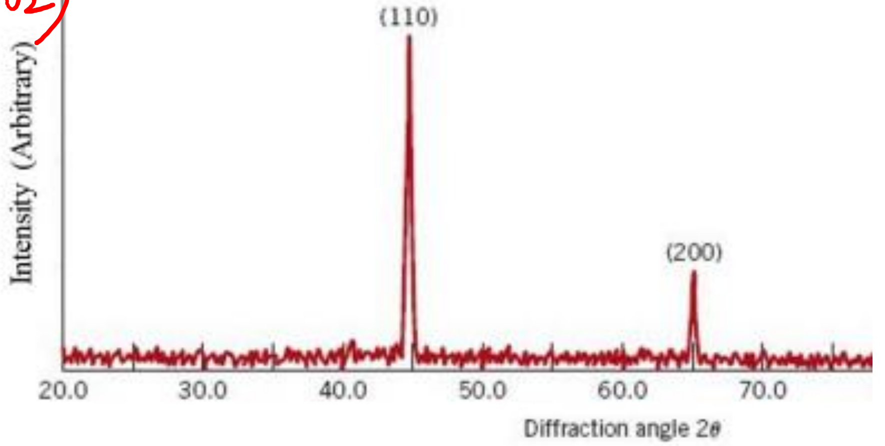
$n\lambda = 2(d_{001})\sin\theta$

$n\lambda = 2(2\cdot d_{002})\sin\theta$

$n\left(\frac{\lambda}{2}\right) = 2\cdot d_{002}\sin\theta$

- Simple cubic crystal, 100, 200, 300… are all allowed 'reflections' -----> no atoms in the planes lying *within* the unit cell.

- BCC: an atom is present also in the (0 0 2) plane.



Structure factor

$$F_{hkl} = \sum_{i=1}^{n} f^{i} . e^{2\pi i(hx_i + kx_i + lx_i)}$$

Electronic property of atom

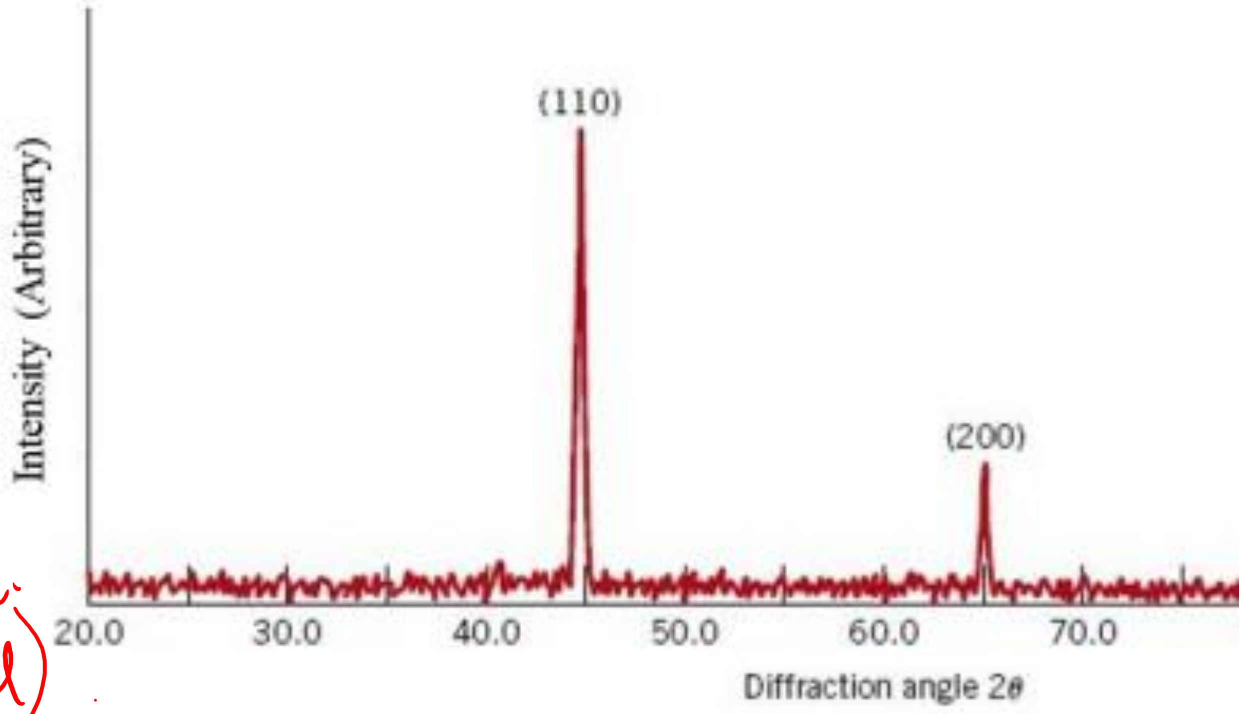
structural property of atom

BCC

M1

M2

d-spacing → e^- contribu
(or equipotential)



Systematic absences (Extinction rules)

- *Even if Bragg's equation is satisfied, 'reflections may go missing'*
  $\rightarrow$ *this is due to the presence of additional atoms in the unit cell.*

Bravais Lattice	**Allowed reflections**	**Necessarily absent reflections**
Simple	all	None
Body centred	(h + k + l) even	(h + k + l) odd
Face centred	h, k and l unmixed *(all even or all odd)*	h, k and l mixed
End centred *(C-centred)*	h and k unmixed	h and k mixed

Suppose an unknown sample is irradiated using the monochromatic X-ray produced from the Cu target ($\lambda_{Cu_{K_{\alpha_1}}}$ = 1.5418 Å)

- Determine the crystal structure.
- Determine the lattice parameter.

- Braggs equation: $$\lambda = 2dSin\theta$$

- Relation between interplanar distance and lattice parameter for a cubic crystal: $$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

- Rearranging the terms: $$\lambda^2 = \frac{4a^2 \sin^2 \theta}{h^2 + k^2 + l^2}$$

- The LHS of the equation is a constant, and therefore, the RHS should also be a constant: $$\frac{\lambda^2}{4a^2} = \frac{\sin^2 \theta}{h^2 + k^2 + l^2}$$

You will get the 2θ values

Generate a set of $\sin^2\theta$ values

Normalize the $\sin^2\theta$ values by generating $\frac{\sin^2\theta_2}{\sin^2\theta_1}$

Clear fractions from normalized values

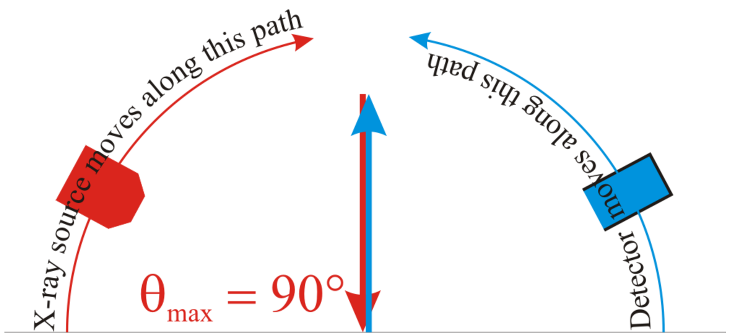
Speculate the h,k,l values such that $(h^2+k^2+l^2)$ = clear fraction column

2θ
44.48
51.83
76.35
92.9
98.4
121.87
144.54
155.51

$$\frac{\lambda^2}{4a^2} = \frac{\sin^2\theta}{h^2+k^2+l^2}$$

$\lambda_{Cu_{K_{\alpha_1}}}$ = 1.5418 Å

You will get the 2θ values	Generate a set of $\sin^2\theta$ values	Normalize the $\sin^2\theta$ values by generating $\frac{\sin^2\theta_2}{\sin^2\theta_1}$	Clear fractions from normalized values	Speculate the h,k,l values such that $(h^2+k^2+l^2)$ = clear fraction column	
2θ	**$\sin^2\theta$**	$\frac{\sin^2\theta_2}{\sin^2\theta_1}$	**$(h^2+k^2+l^2)$**	**(h k l)**	$\frac{\sin^2\theta}{(h^2+k^2+l^2)}$
44.48	0.143	1	3	1 1 1	0.0477
51.83	0.191	1.34	4	2 0 0	0.0478
76.35	0.382	2.67	8	2 2 0	0.0477
92.9	0.525	3.67	11	3 1 1	0.0477
98.4	0.573	4.01	12	2 2 2	0.0477
121.87	0.764	5.34	16	4 0 0	0.0477
144.54	0.907	6.34	19	3 3 1	0.0477
155.51	0.955	6.68	20	4 2 0	0.0477



$$\frac{\lambda^2}{4a^2} = \frac{\sin^2\theta}{h^2+k^2+l^2}$$

$\lambda_{Cu_{K\alpha_1}}$ = 1.5418 Å

Allowed reflections in SC, BCC, FCC and DC crystals

Cannot be expressed as $(h^2+k^2+l^2)$

$h^2 + k^2 + l^2$	SC	FCC	BCC	DC
1	100			
2	110		110	
3	111	111		111
4	200	200	200	
5	210			
6	211		211	
7				
8	220	220	220	220
9	300, 221			
10	310		310	
11	311	311		311
12	222	222	222	
13	320			
14	321		321	
15				
16	400	400	400	400
17	410, 322			
18	411, 330		411, 330	
19	331	331		331

Determination of lattice parameter of a crystal

Crystal with atoms

Diffraction experiment

Crystal to 2θ

2θ information (*Intensity-2θ plot*)

Missing reflections

Get lattice type (SC, BCC, FCC,...)

2θ to 'd'

Bragg's equation

$$n\,\lambda_{Cu\,K\alpha} = 2\,d_{(hkl)}\,\mathrm{Sin}\,\theta_{hkl}^{Bragg}$$

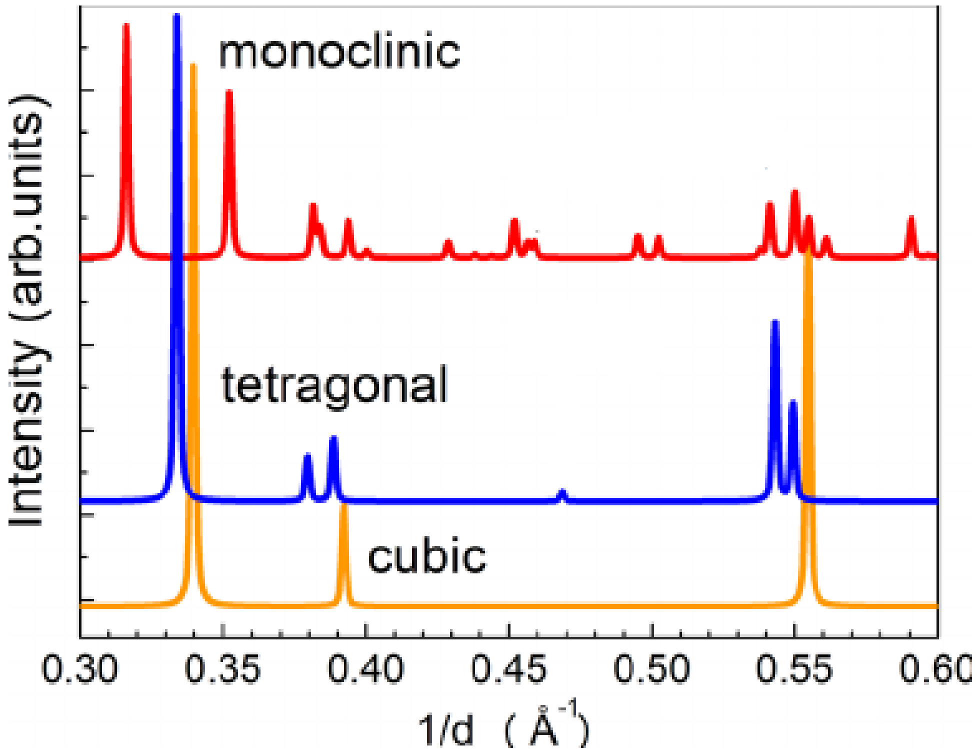
Get 'd' spacing

Equation connecting 'd' to 'a' (lattice parameter)

$$d_{(hkl)}^{Cubic\ crystal} = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

'd' to 'a'

Get 'a' (lattice parameter)



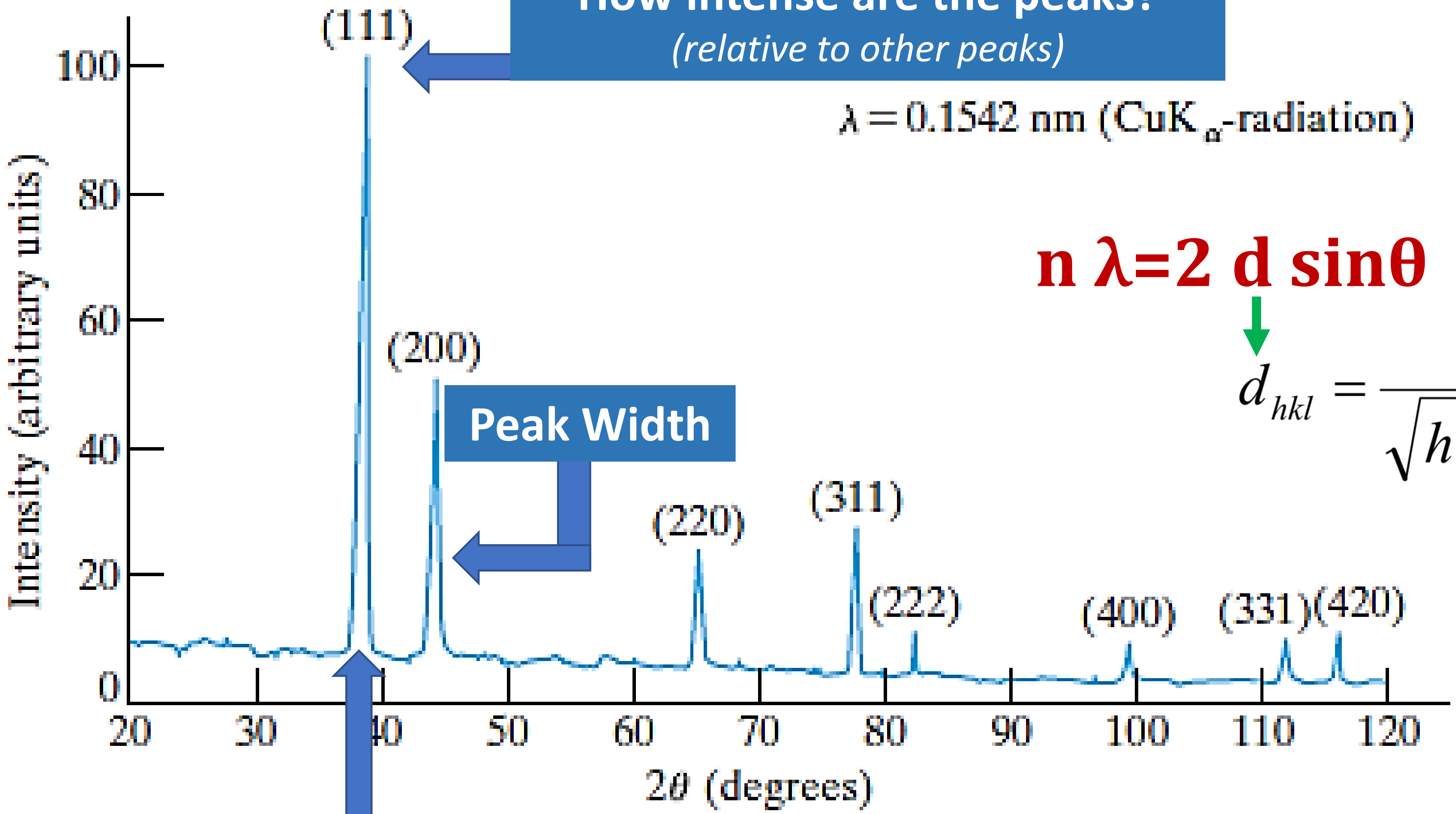
- Lower the symmetry of the crystal, more the number of peaks (e.g., in tetragonal crystal the 100 peak will lie at a different 2θ as compared to the 001 peak).

- Lattice type ➢ in SC we will get more peaks as compared to (say) FCC

- Smaller the wavelength of the X-rays, more will be the number of peaks possible.

Peak characteristics in XRD

How intense are the peaks?
(relative to other peaks)



$\lambda = 0.1542$ nm (CuK_{α}-radiation)

Peak Width

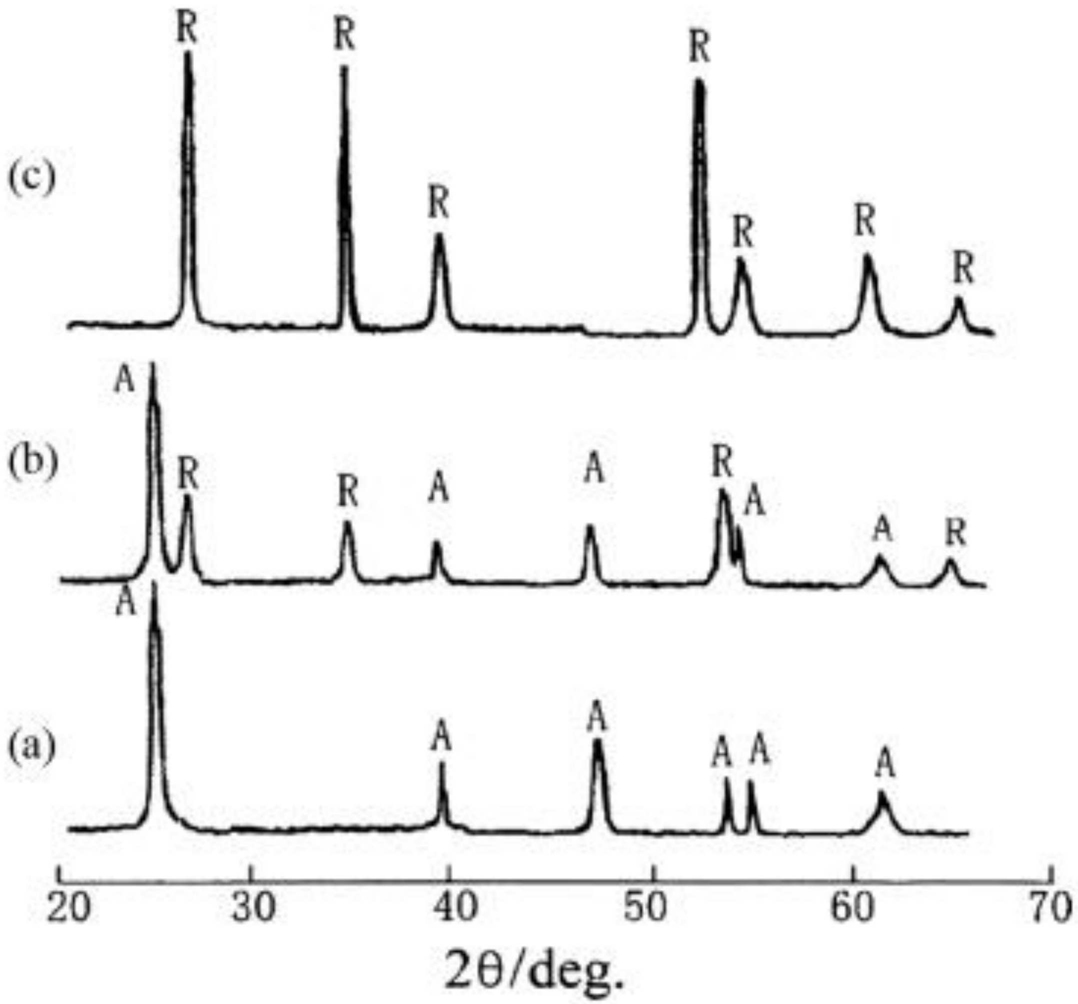
Peak Position

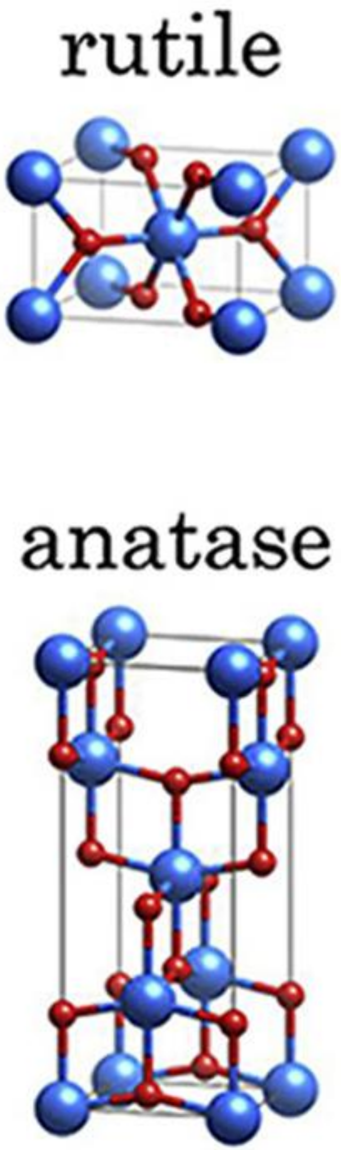
$$n\,\lambda = 2\,d\,\sin\theta$$

$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}$$

How can the peak position be changed for a given material?

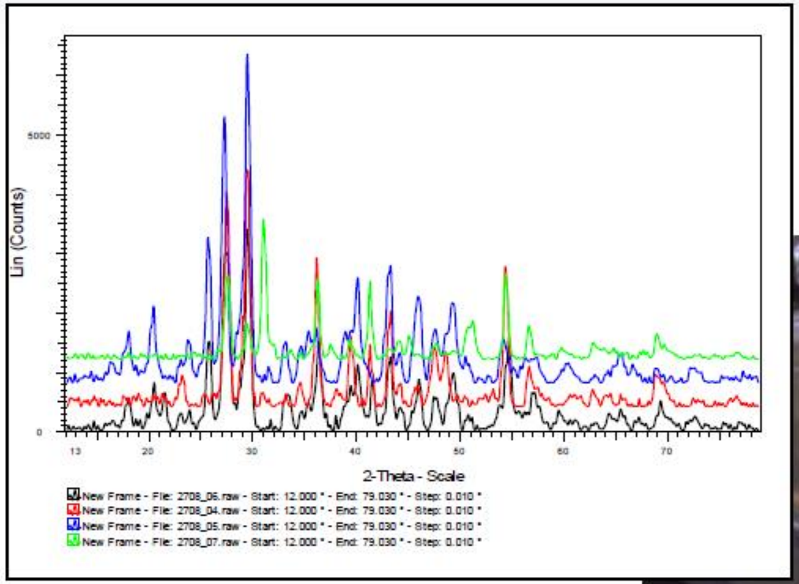
Polymorphism





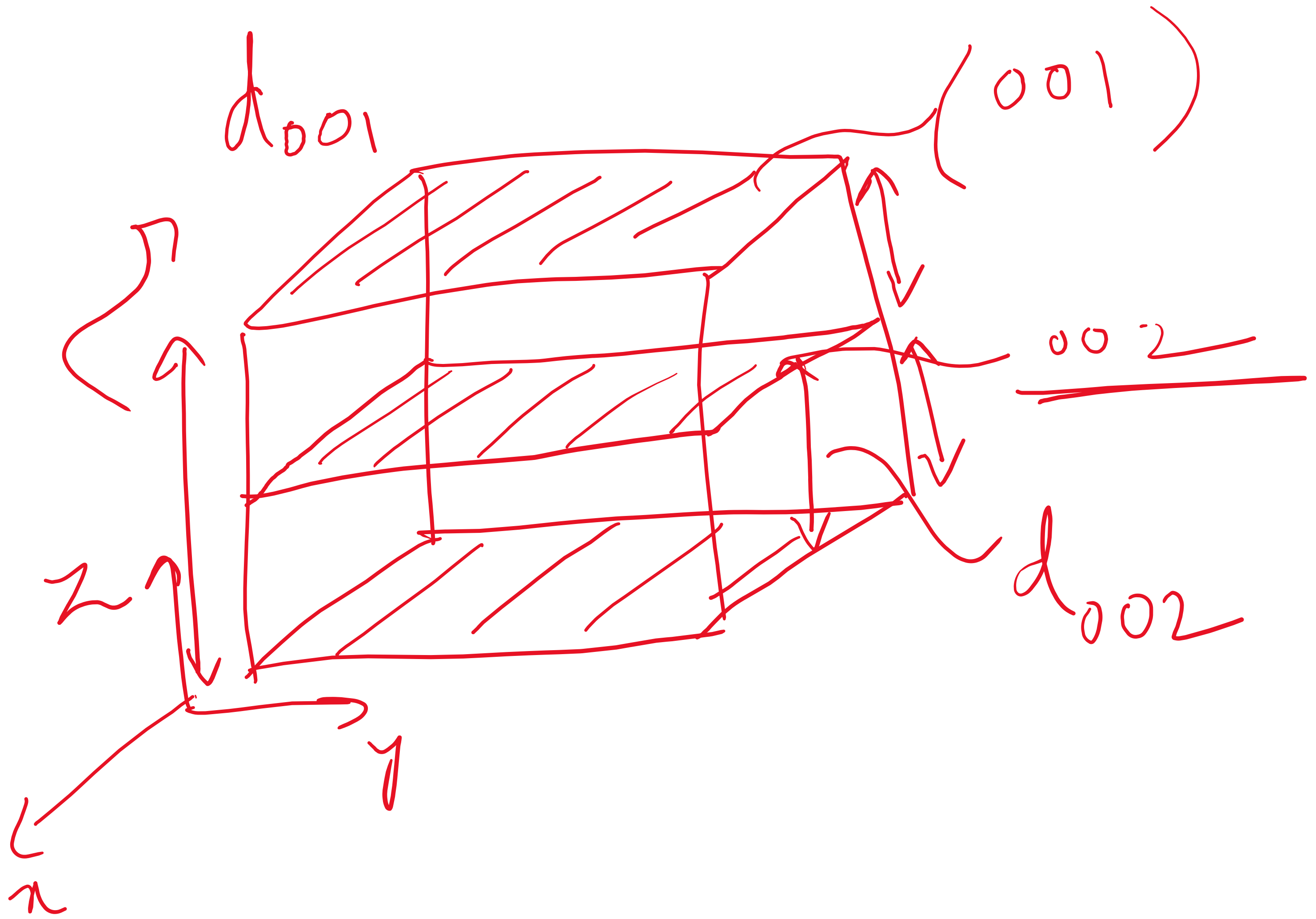
H. Ijadpanah-Saravy , M. Safari , A. Khodadadi-Darban & A. Rezaei (2014) Synthesis of Titanium Dioxide Nanoparticles for Photocatalytic Degradation of Cyanide in Wastewater, Analytical Letters, 47:10, 1772-1782

Forensic Sciences



sequence of coatings is
characteristic of car type

- Paint chips are transferred in car accidents, either from one car to another or, in the case of a hit-and-run, from the car to the victim.
- Chemical identity of the various layers of the paints



d_{001}
(001)
002
d_{002}
z
y
x

Quiz 1: Announcement

Total marks of Quiz: 10 (multiple choice type- only one option will be correct),
Negative marking: NO
Time for the quiz: 15 min, Start time: January 25, 2022, 10:30 a.m. (IST), Finish Time: January 25, 2022, 10:45 a.m. (IST).

Important note:

1) Quiz-1 will start at 10:30 a.m. (IST) sharp on 25th January.
2) Keep pen, pencil, calculator nearby to you. There may be numerical questions, you may have to calculate.
3) Kindly login to your Moodle account at least **10 min before the schedule, preferably 10:20 a.m. or before.**
4) **Password of the quiz will be sent to your email id 3-5 min before the quiz starts**. Around 10:25 a.m., password will be shared. You should login your email account at 10:20 a.m. and be vigilant.
5) Total time of the quiz will be 15 mins. You cannot attempt the quiz anymore after 10:45 a.m. (IST).
6) **The questions will appear in sequential order. Therefore, you cannot go back to the previous question once you move forward.**
7) Any kind of act of group cheating through WhatsApp chats or any other internet forum is highly discouraged (as mentioned in the class). Strong disciplinary actions will be taken if found guilty which may result disqualifying from the entire course in other words failing in the course.
8) No re-quiz request will be entertained. Make sure you attend it at any cost. This point is same for all the exams in this course.
9) **Result of the quiz will be visible to you on 27th January, 2022. Before that no request regarding quiz results will be entertained.**

MLL 100

Introduction to Materials Science and Engineering

Lecture-9 (January 21, 2022)

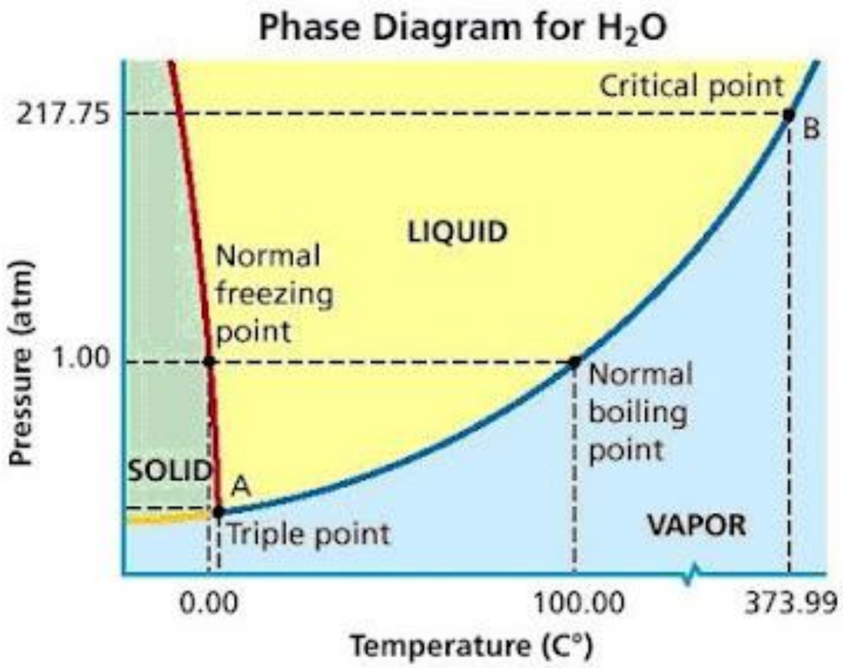
Dr. Sangeeta Santra (*ssantra@mse.iitd.ac.in*)

IIT Delhi
Department of Materials Science and Engineering

Phase Equilibrium,
Phase Diagram,
Phase Transformation

Phase diagram

Equilibrium phase diagram: Map of phases represented over state variables.



Phase

Happy

Shocking

Sad

Worrisome

Excited

Funny

Silent

Depressed

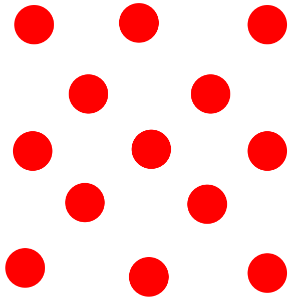
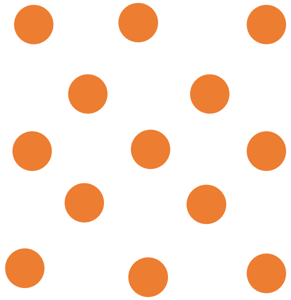
- Physically distinct

- Chemically uniform: water
- Mechanically separable

- In solids, different crystal structures indicate different phases.

Component

Component		Component		Phase	Phase mixture
	+		=		
					

 + = 

What is a component?

- Chemically-independent constituents of a system

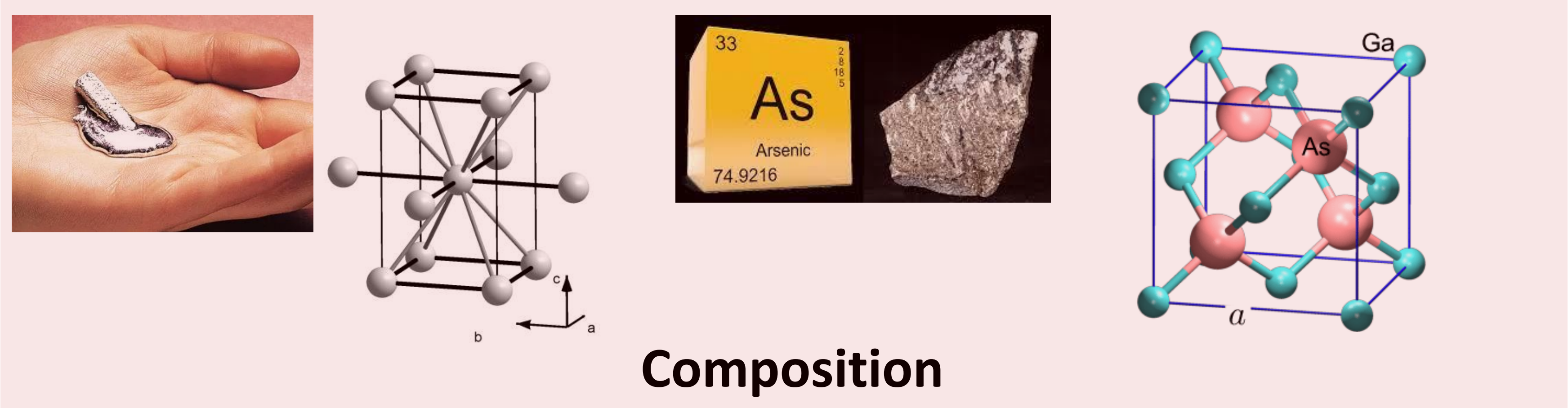
- *Copper-Tin system:* Cu and Sn are the components
- *Sugar-milk system:* Sugar and milk are the components
- *Vanilla-chocolate system:* Vanilla and cocoa are the components
- *SiO_2-Al_2O_3-MgO system:* SiO_2, Al_2O_3, MgO are the components

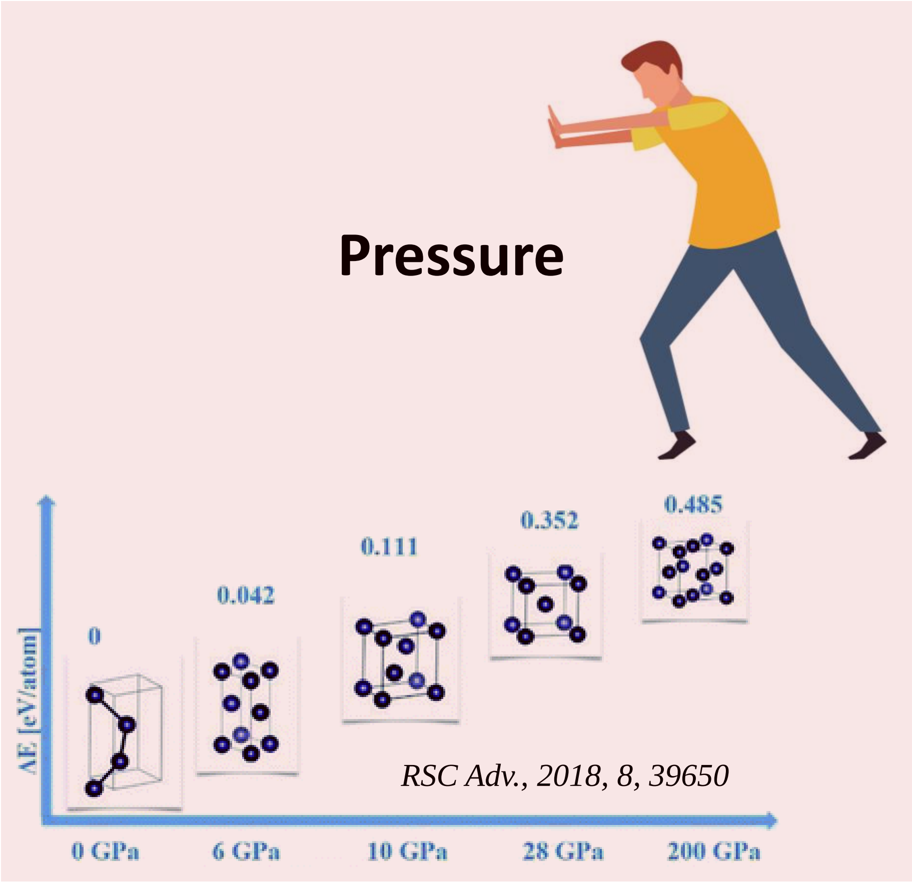
Classification of phase diagrams based on number of components:

- ❑ Unary phase diagram: Water -----> H_2O
- ❑ Binary phase diagram: Cu-Ni
- ❑ Ternary phase diagram: Cu-Ni-Pt
- ❑ Quaternary phase diagram: Cu-Ni-Al-Pt
- ❑ Pseudo-binary phase diagram

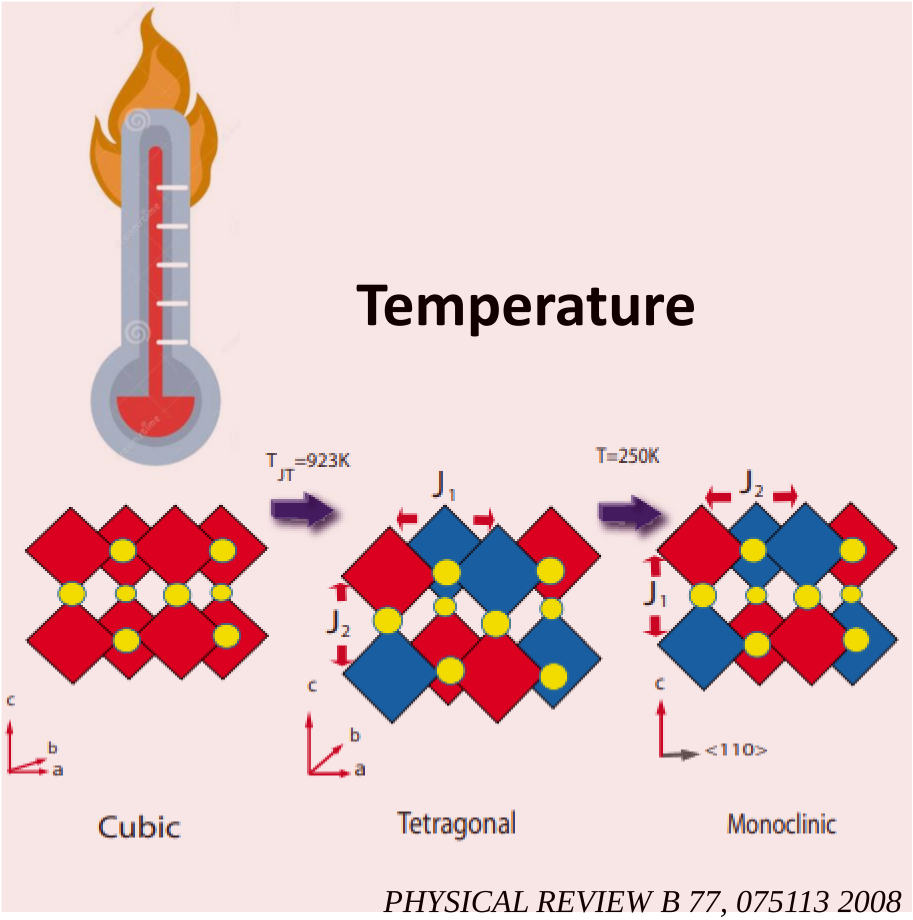
How many components are present in:

(i) Al_2O_3-MgO
(ii) Mg-O
(iii) NaCl-H_2O
(iv) Ni-Al-O

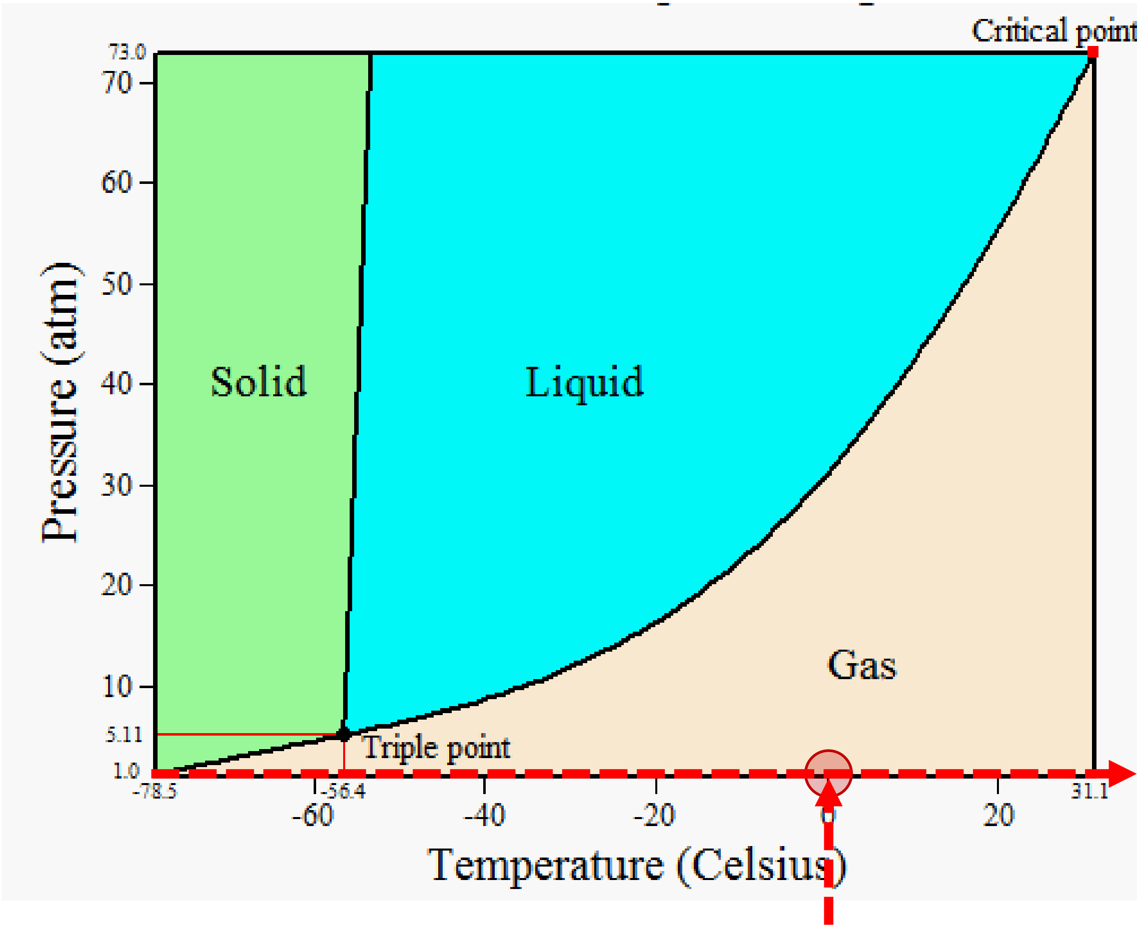




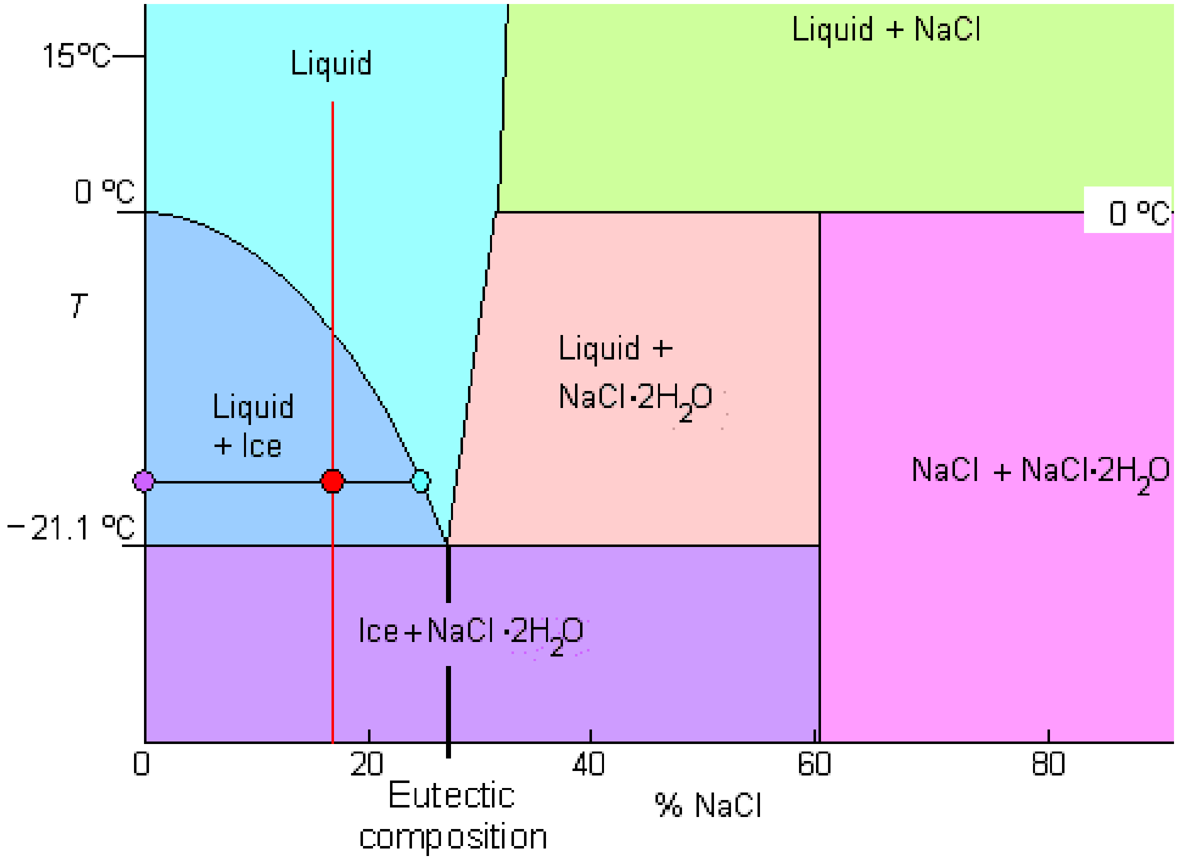
What are the factors affecting the phase formation?



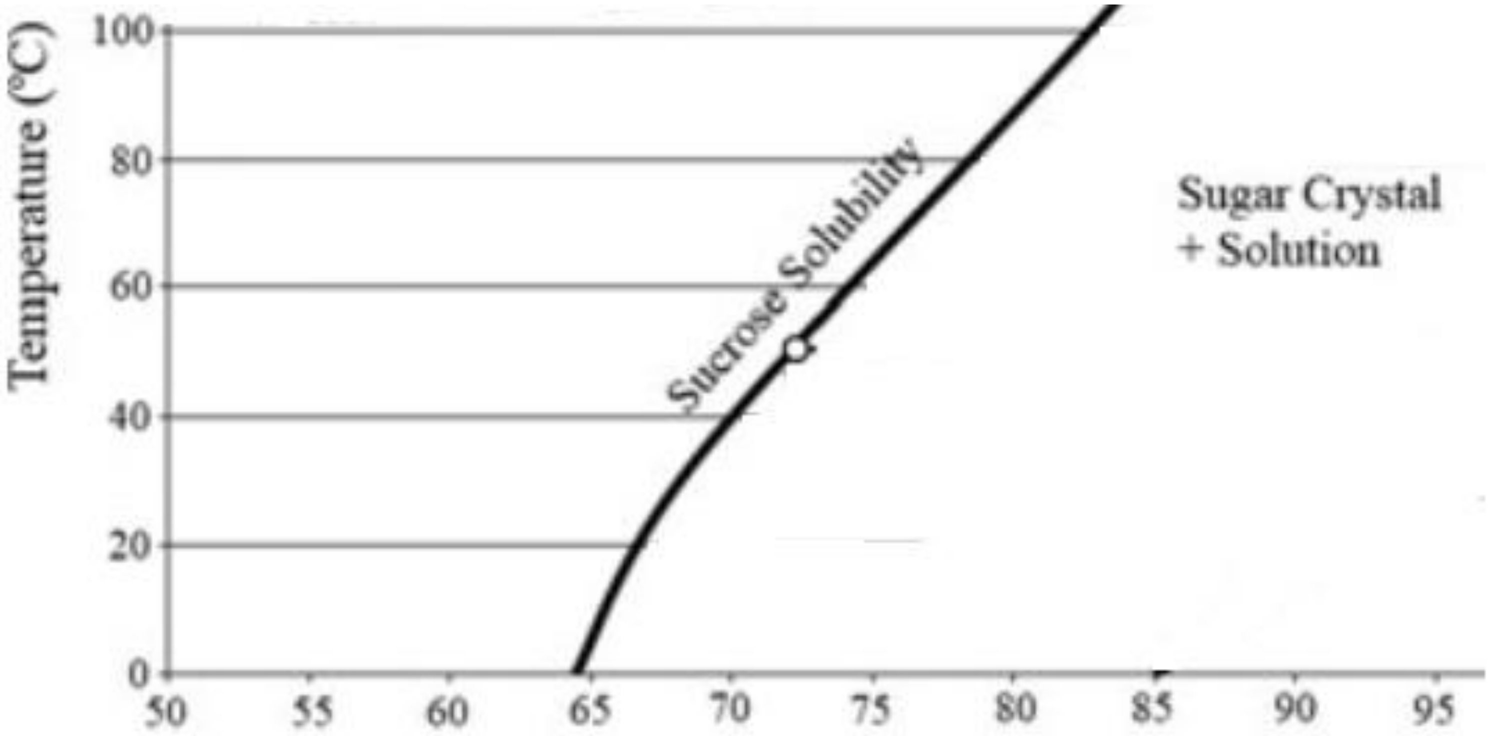
P-T diagram



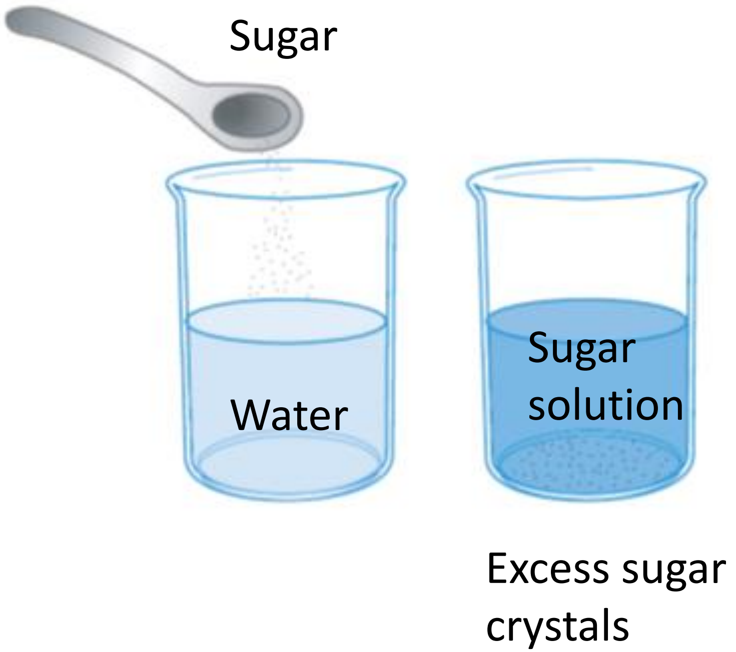
T-C diagram



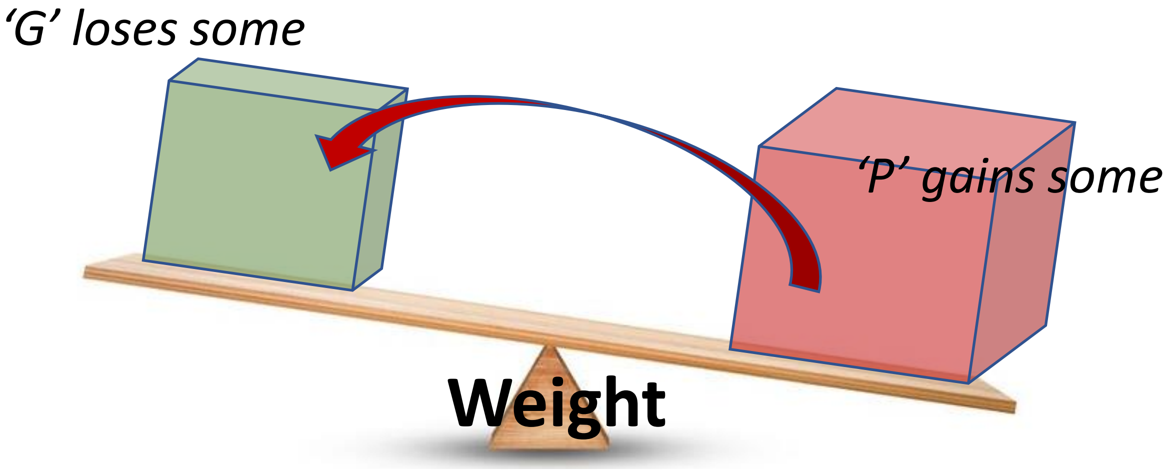
Solubility limit

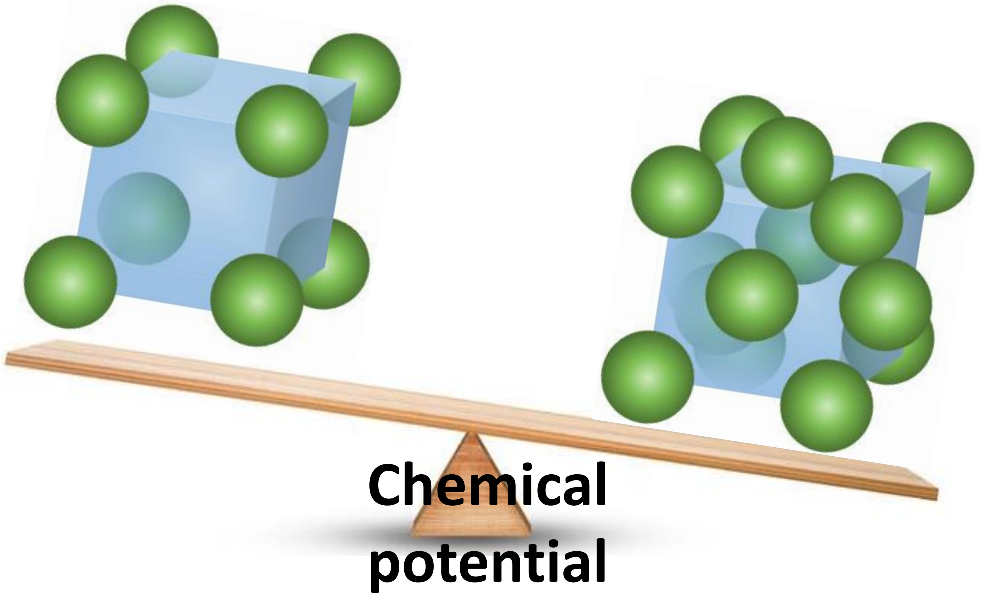


% sugar →
(wt% or at% or vol.)

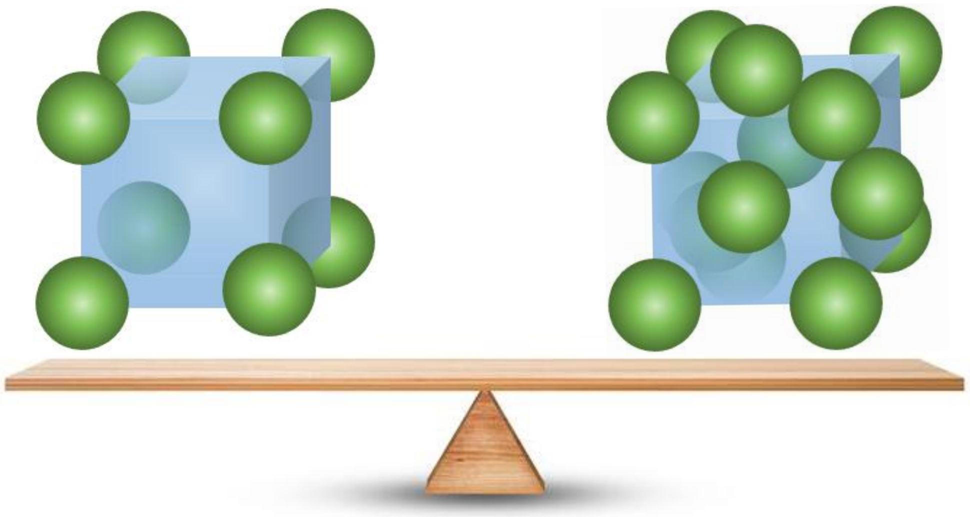


When will be the phases in equilibrium?





- For the phases to be in equilibrium, chemical potential (μ) of the components involved must be equal.



Chemical potential

- Represents a potential for any material to interact in a specific system.

- Change in energy in a system with the change in the number of atoms of a given material.

- High chemical potential: Donate the atoms
- Low chemical potential: Accept the atoms

- If $\alpha, \beta, \gamma, \ldots\ldots., P$ are the phases in equilibrium for a given binary A-B system, then:

$$\mu_A^\alpha = \mu_A^\beta = \mu_A^\gamma = \ldots\ldots\ldots = \mu_A^P$$

$$\mu_B^\alpha = \mu_B^\beta = \mu_B^\gamma = \ldots\ldots\ldots = \mu_B^P$$

Gibb's Phase Rule

- Total number of phases = P $\quad P_1 \quad P_2 \quad P_3 \quad \ldots\ldots\ldots \quad P_P$

- Total number of components = C $\quad C_1 \quad C_2 \quad C_3 \quad \ldots\ldots\ldots \quad C_C$

$$\sum_{i}^{n} C = 1$$

- Independent concentration variables for one phase = C-1

- Other two independent variables = Temperature (T) and Pressure (P) = 2

- Independent concentration variables for P phases = P(C-1) + 2

- Total number of variables = P(C-1) + 2

- Phases present in a system can be in equilibrium when the chemical potential (μ) of each of the component is the same in all phases

$$\mu_A^{\alpha} = \mu_A^{\beta} = \mu_A^{\gamma} = \ \dots\dots\dots = \mu_A^{P}$$

$$\mu_B^{\alpha} = \mu_B^{\beta} = \mu_B^{\gamma} = \ \dots\dots\dots = \mu_B^{P}$$

- Total number of equilibria for ‘C’ components = C (P-1)

- Total degree of freedom = Total number of variables – Total number of equilibria

Total degree of freedom = P(C-1) + 2 – C (P-1) = PC - P + 2 – CP + C = C - P + 2

Gibbs Phase Rule

- Gives information about the conditions of phase equilibrium in different systems.

$$\underbrace{F}_{\text{Degree of freedom}} = \underbrace{C}_{\text{No. of components}} - \underbrace{P}_{\text{No. of phases}} + \underbrace{2}_{\text{Variables } (T,\, P)}$$

MLL 100

Introduction to Materials Science and Engineering

Lecture-10 (January 28, 2022)

Dr. Sangeeta Santra (*ssantra@mse.iitd.ac.in*)

IIT Delhi
Department of Materials Science and Engineering

What have we learnt in Lecture-9?

- ❑ Component
- ❑ Phase
- ❑ Phase diagram
- ❑ Phase equilibrium
- ❑ Chemical potential
- ❑ Gibb’s phase rule

Gibb's phase rule

- Gives information about the conditions of phase equilibrium in different systems.

$$F = C - P + 2$$

Degree of freedom

No. of components

No. of phases

Variables (*T, P*)

Phases

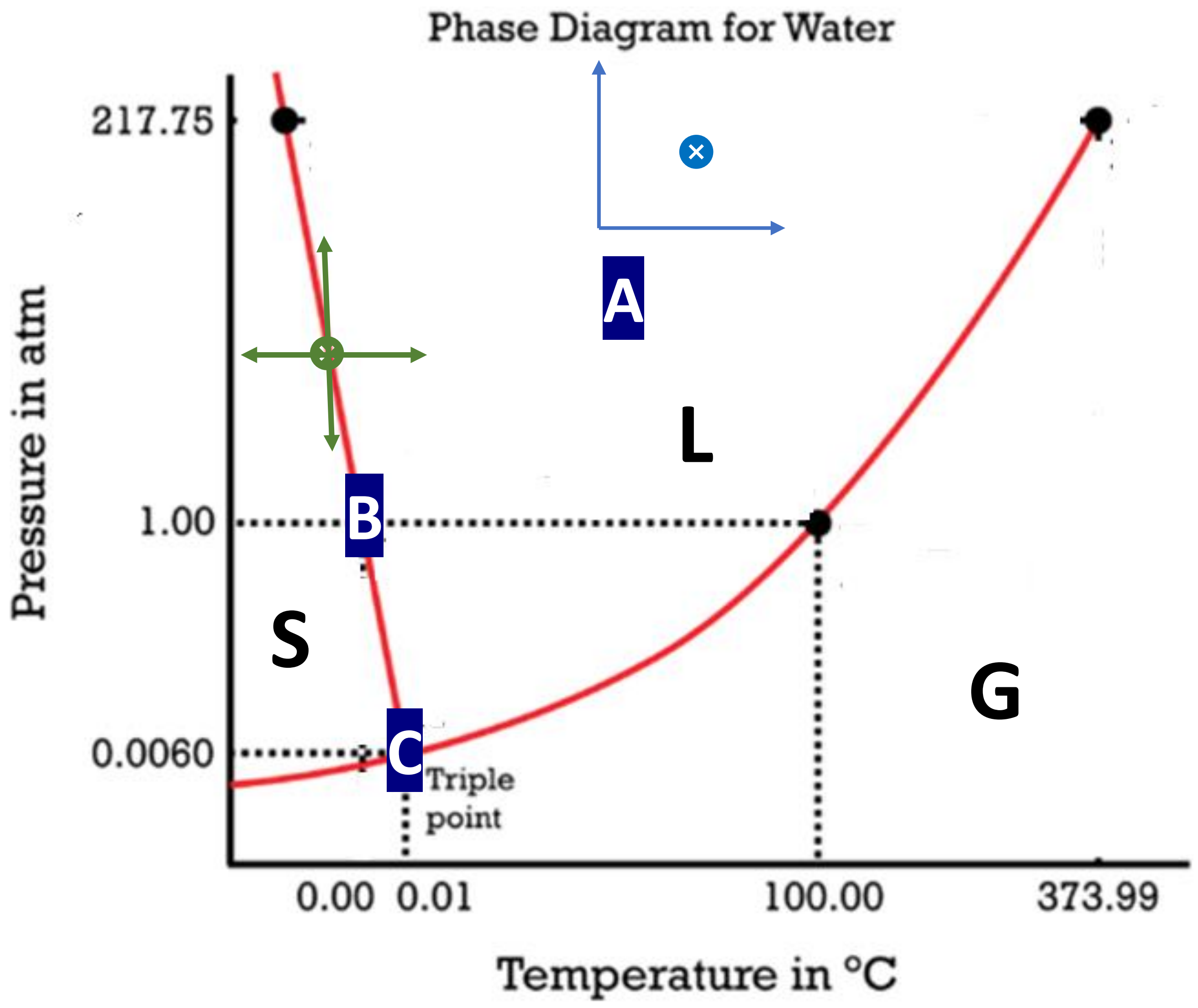
→ Different crystal structures (Same component)

→ Different states of matter

→ Same crystal structure; but two different elements / components

Cu, Ni → FCC

Single-component system



A

C = 1

P = 1

F = 1-1+2 = 2

Both T and P can be varied independently, still will be in 'L' phase.

B

C = 1

P = 2

F = 1-2+2 = 1

Either T and P can be varied independently.

C

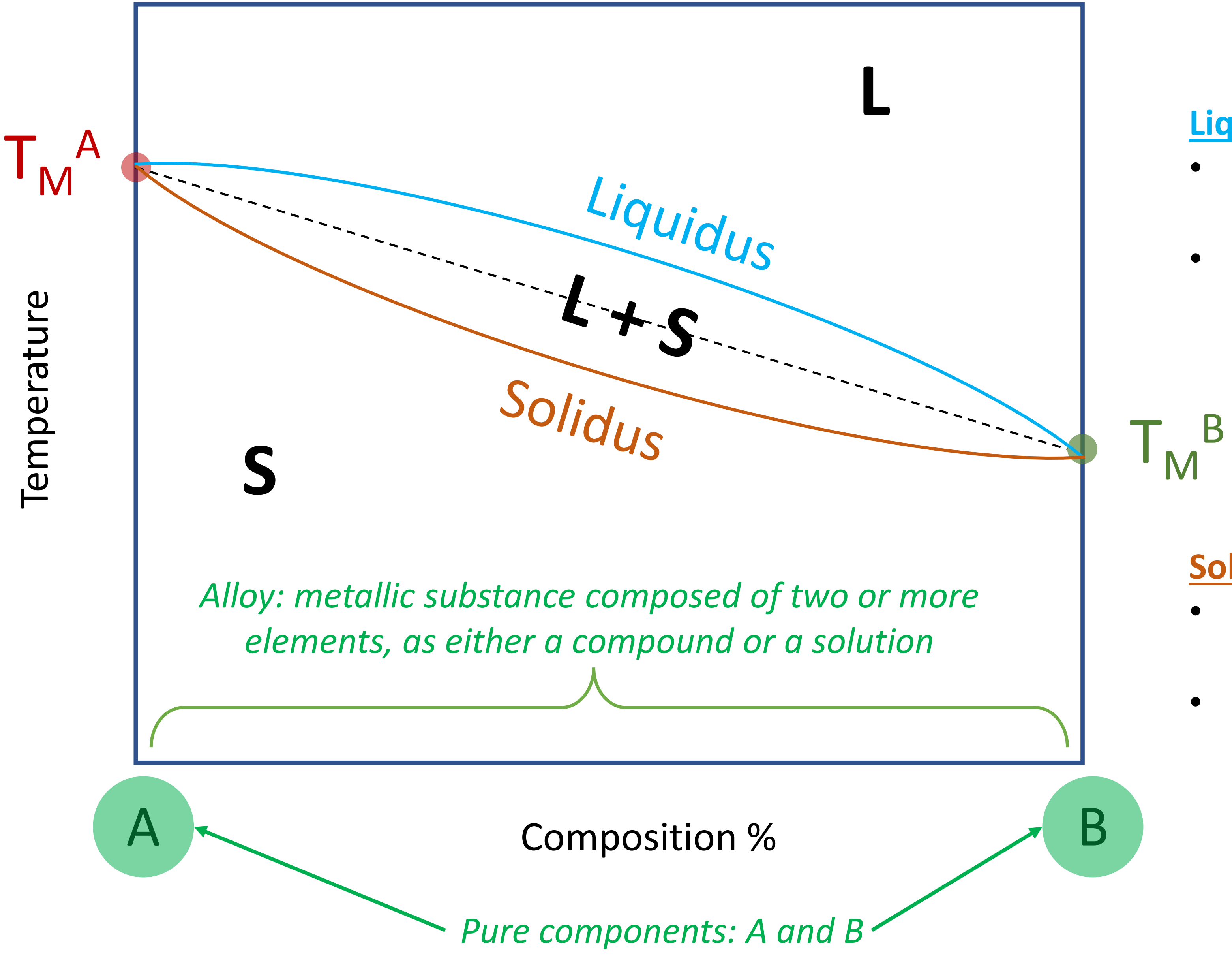
C = 1

P = 3

F = 1-3+2 = 0

Neither T and P can be varied independently.

Binary system *(Pressure is constant)*



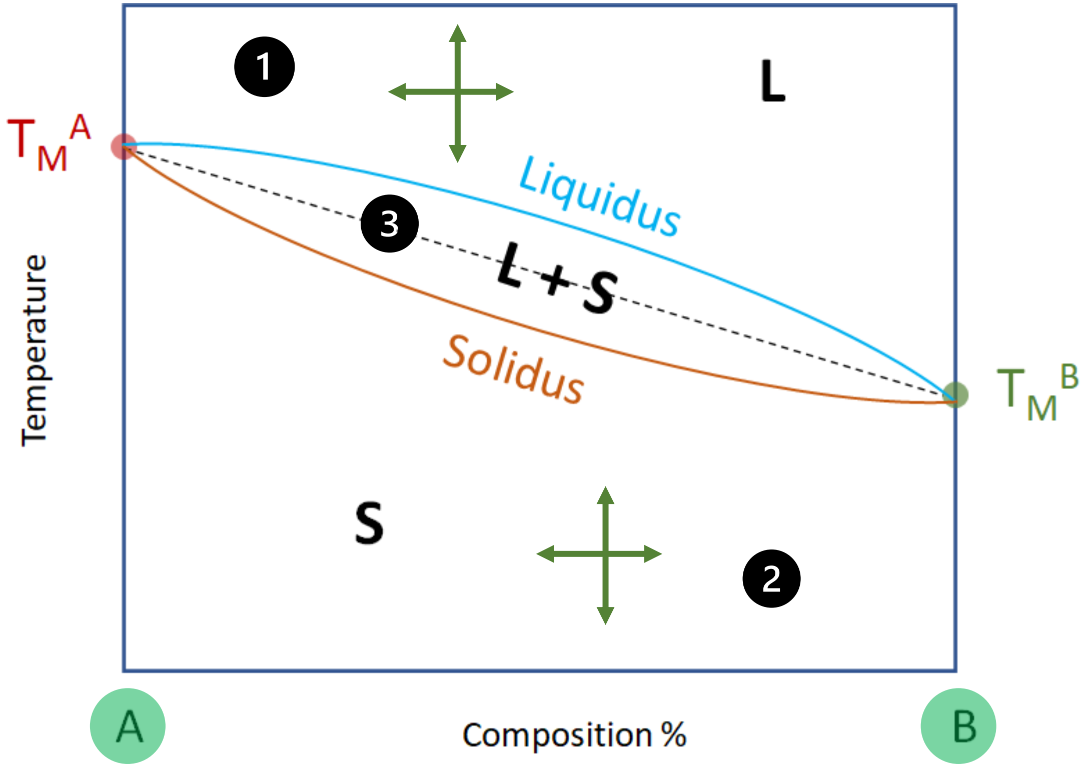
Liquidus:

- Temperature above which the alloy is completely liquid.
- Below Liquidus, solidification starts.

Solidus:

- Temperature below which the alloy is completely solid.
- Above solidus, liquefaction starts.

Condensed Gibb's phase rule *(Pressure is constant)*



$$F = C - P + 1$$

- Pressure is constant.
- '1' stands for the state variable: Temperature.

1

C = 2 (A and B)

P = 1 (Liquid)

F = 2-1+1 = 2

- Both T and C can be varied independently, still will be in 'L' phase.

2

C = 2 (A and B)

P = 1 (Solid)

F = 2-1+1 = 2

- Both T and C can be varied independently, still will be in 'S' phase.

3

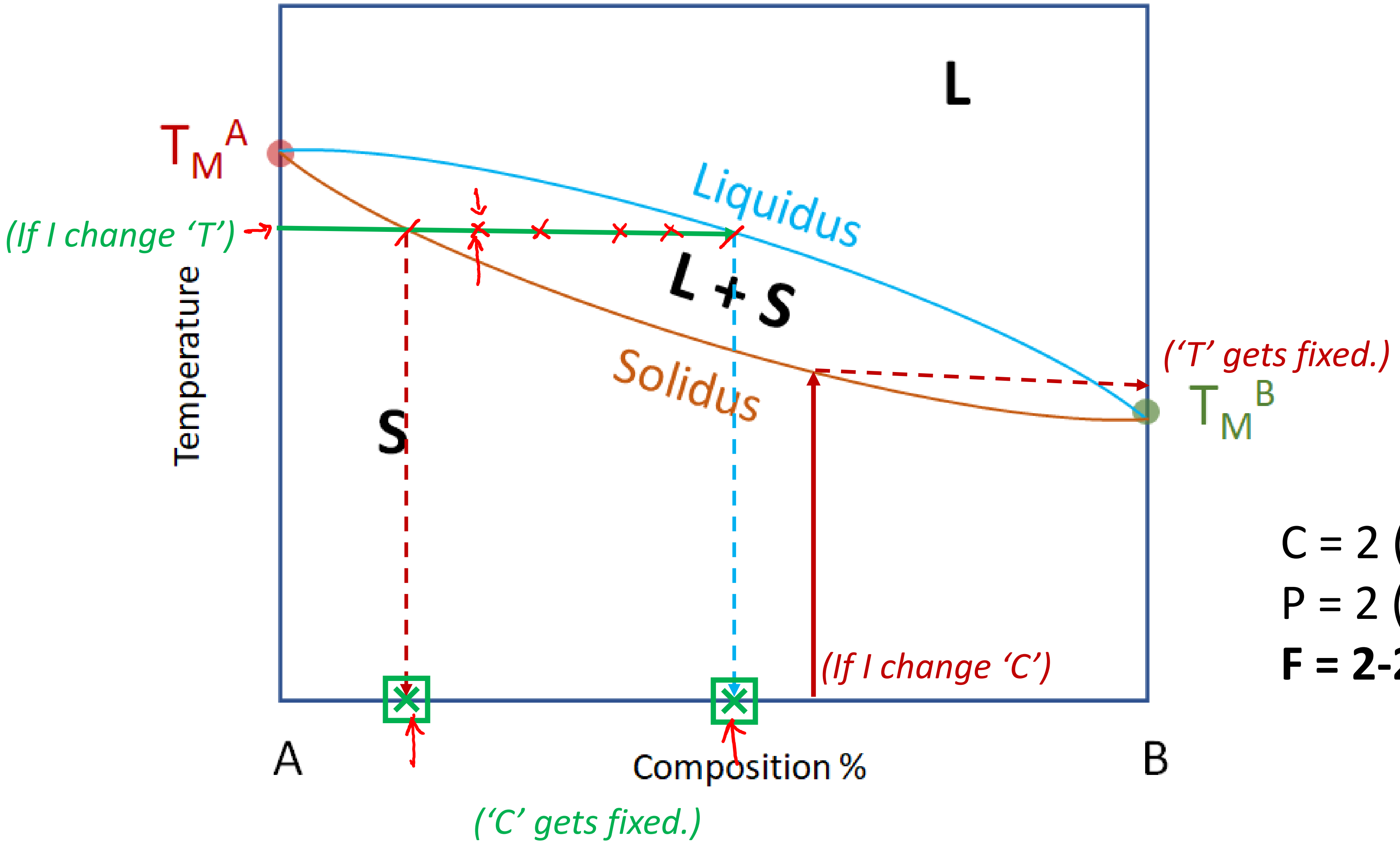
C = 2 (A and B)

P = 2 (Liquid + Solid)

F = 2-2+1 = 1

- Either T or C can be varied independently, only then 'L+S' two-phase will be in equilibrium.

❸ Anywhere within the two-phase region (L + S)



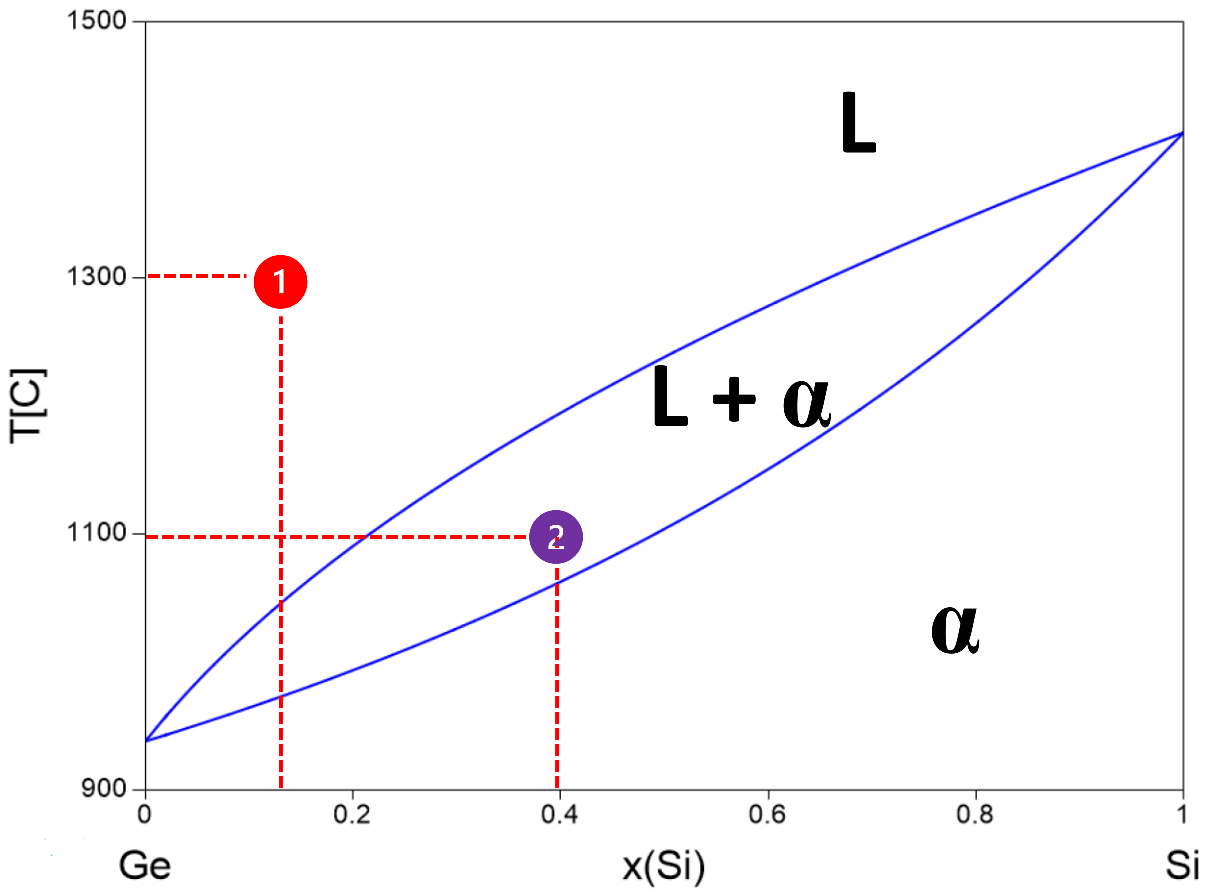
C = 2 (A and B)

P = 2 (Liquid + Solid)

F = 2-2+1 = 1

- Either T or C can be varied independently, only then 'L+S' two-phase will be in equilibrium.

Isomorphous phase diagram



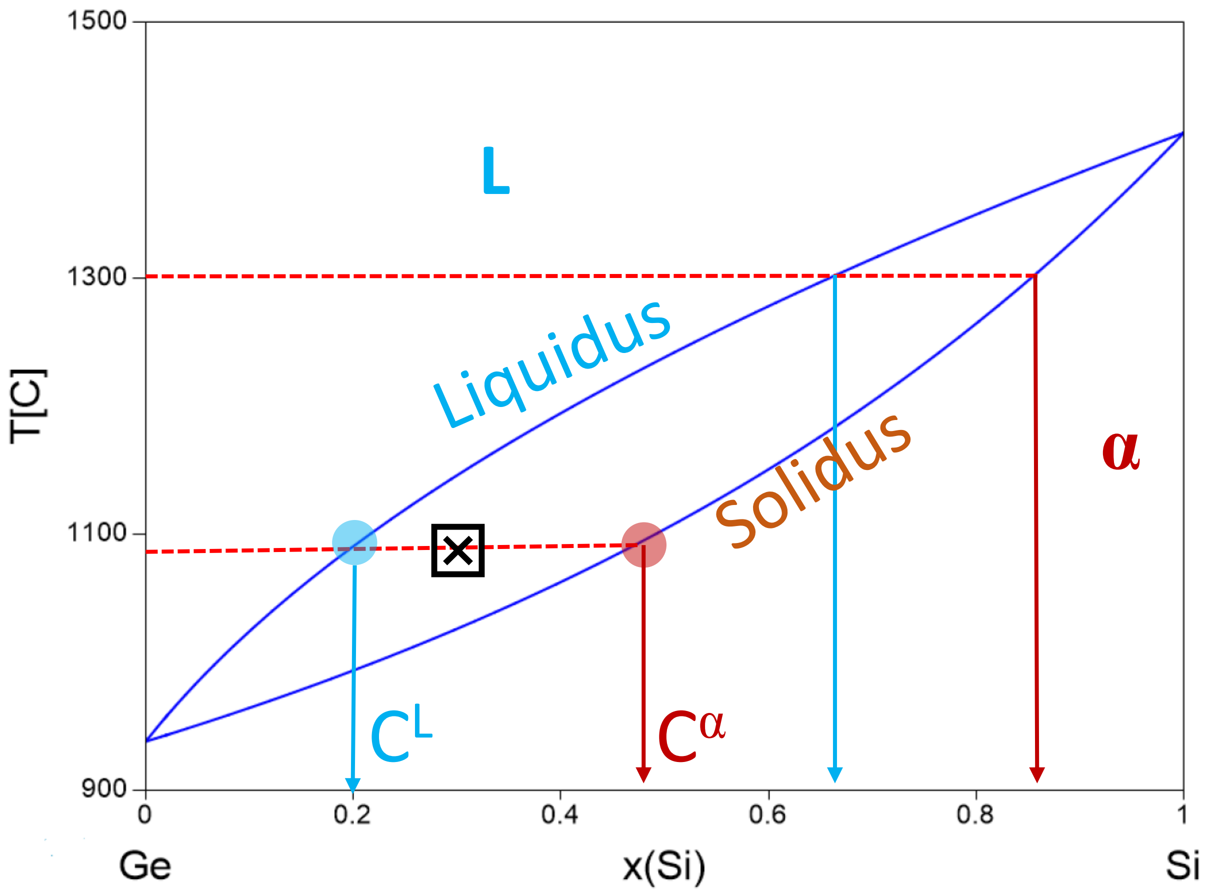
- ❑ Which phases are in equilibrium?

  (Temperature and Composition)

1 Phase: Liquid (L)

2 Phase: Liquid (L) + α

Tie-line

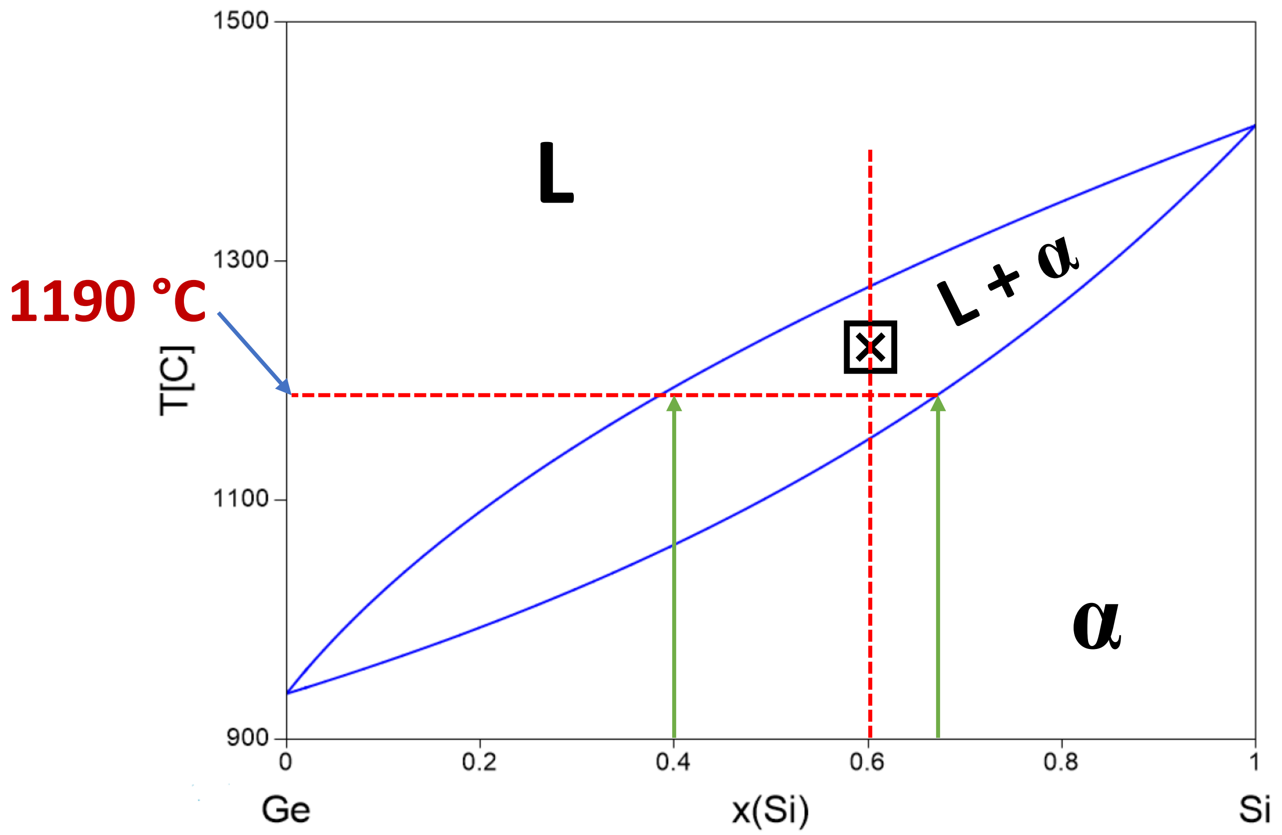


- What are the composition of phases in equilibrium?

C^L : Composition of liquid phase

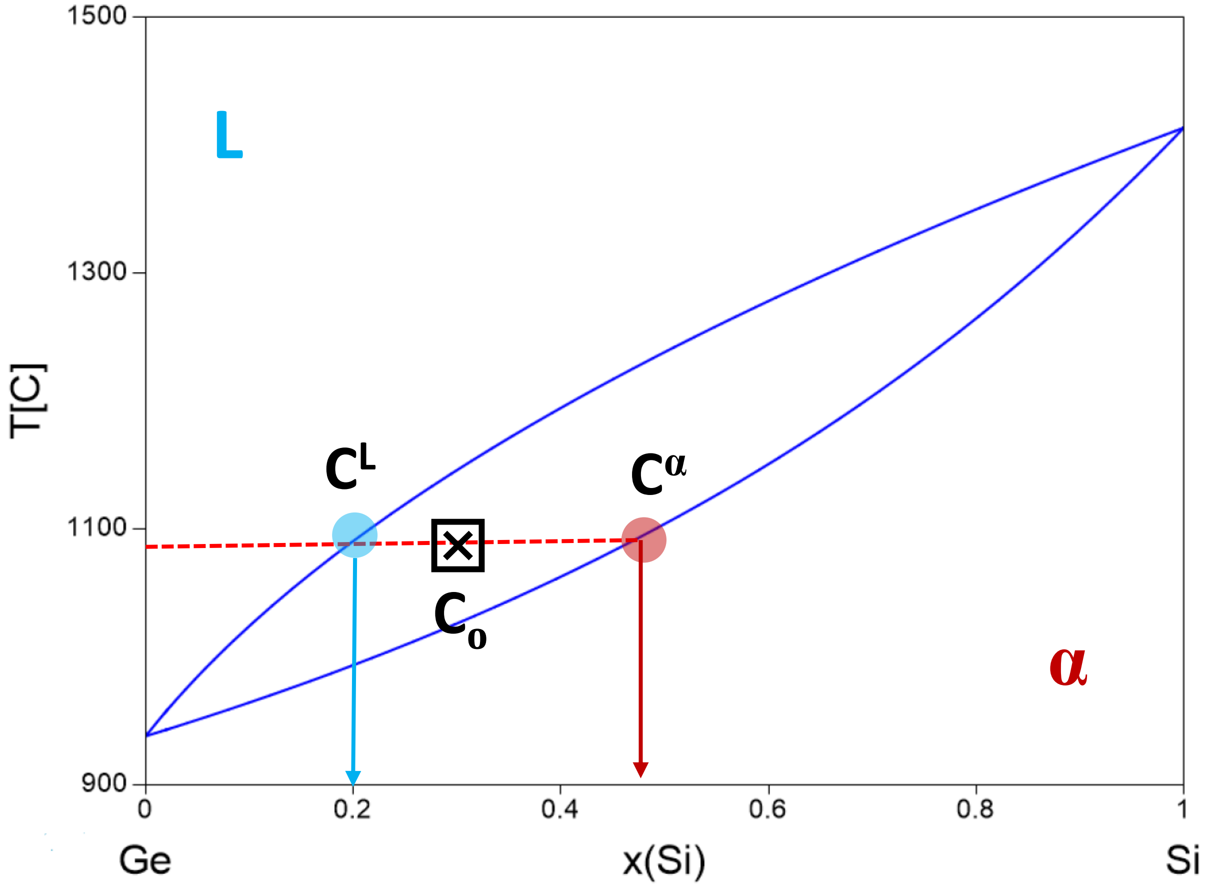
C^α : Composition of α phase

An alloy with an average composition, C_o = 0.6 % Si has two phases in equilibrium. The composition of the phases, L and α are 0.40 and 0.67 % Si respectively. At what temperature is such an alloy stable?



Lever rule

C_o : average composition of alloy



- In what fraction are the phases present?

$$\frac{f_L}{f_\alpha} = ?$$

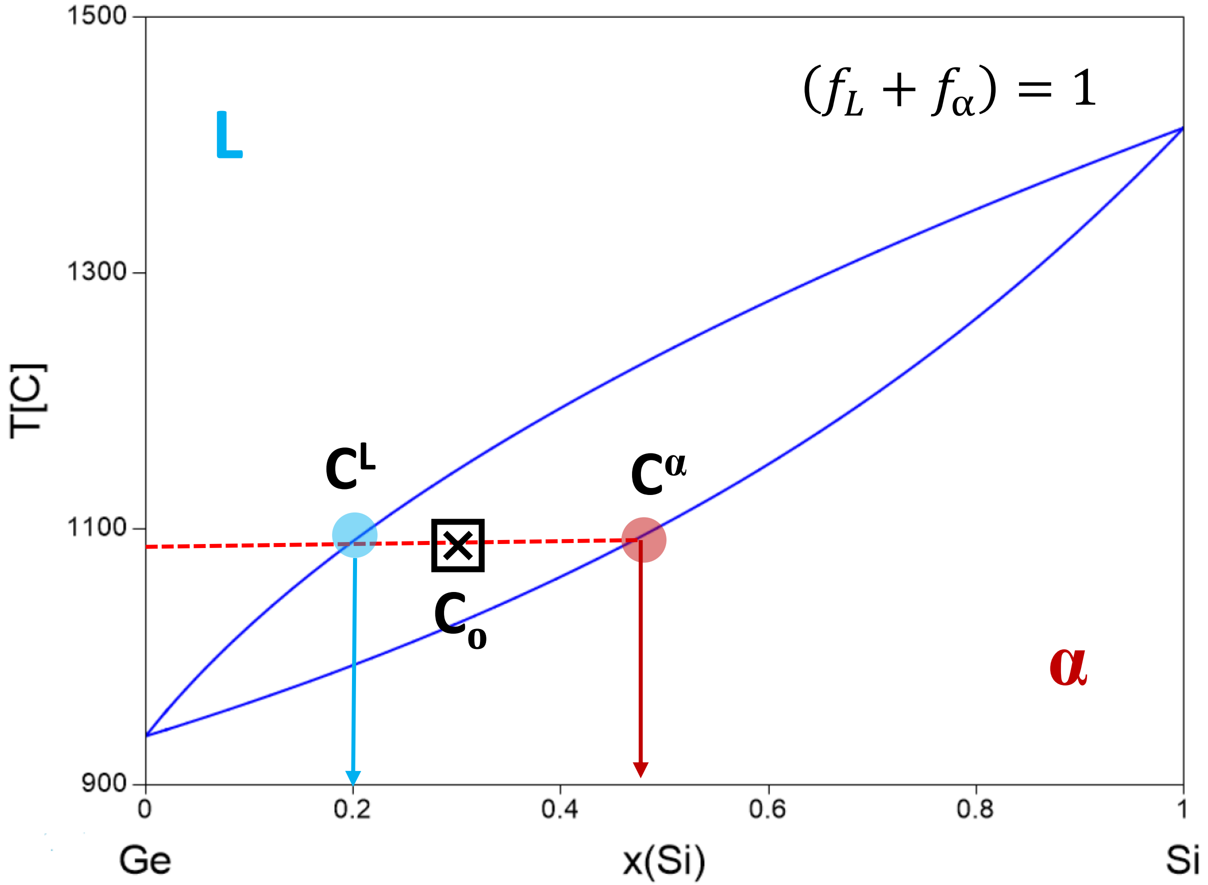
$$f_L . C^L + f_\alpha . C^\alpha = (f_L + f_\alpha) . C_o$$

$$\frac{f_L}{f_\alpha} . C^L + 1 . C^\alpha = \left(\frac{f_L}{f_\alpha} + 1\right) . C_o$$

$$\frac{f_L}{f_\alpha} = \frac{(C_o - C^\alpha)}{(C^L - C_o)}$$

Lever rule

C_o : average composition of alloy



$$f_\alpha = \frac{(C^L - C_o)}{(C^L - C^\alpha)} \qquad f_L = \frac{(C_o - C^\alpha)}{(C^L - C^\alpha)}$$

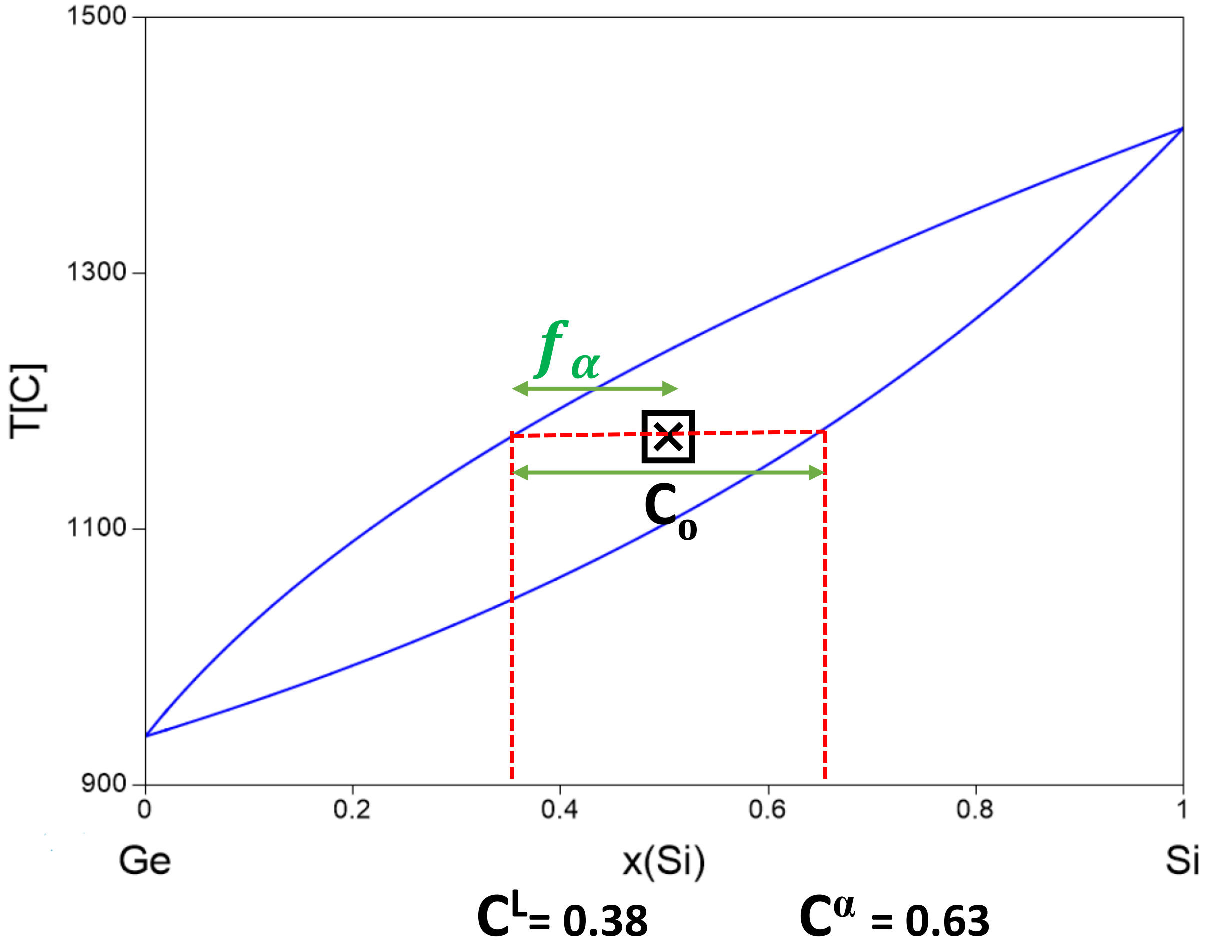
- In what fraction are the phases present?

$$\frac{f_L}{f_\alpha} = \frac{(C_o - C^\alpha)}{(C^L - C_o)}$$

$$1 + \frac{f_L}{f_\alpha} = 1 + \frac{(C_o - C^\alpha)}{(C^L - C_o)}$$

$$\frac{f_\alpha + f_L}{f_\alpha} = \frac{(C^L - C_o) + (C_o - C^\alpha)}{(C^L - C_o)}$$

$$\frac{1}{f_\alpha} = \frac{(C^L) - (C^\alpha)}{(C^L - C_o)}$$



$$f_\alpha = \frac{(C^L - C_o)}{(C^L - C^\alpha)} = \frac{(0.38 - 0.50)}{(0.38 - 0.63)} = 0.48$$

$$f_L = \frac{(C_o - C^\alpha)}{(C^L - C^\alpha)} = \frac{(0.50 - 0.63)}{(0.38 - 0.63)} = 0.52$$

MLL 100

Introduction to Materials Science and Engineering

Lecture-11 (January 29, 2022)

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Department of Materials Science and Engineering

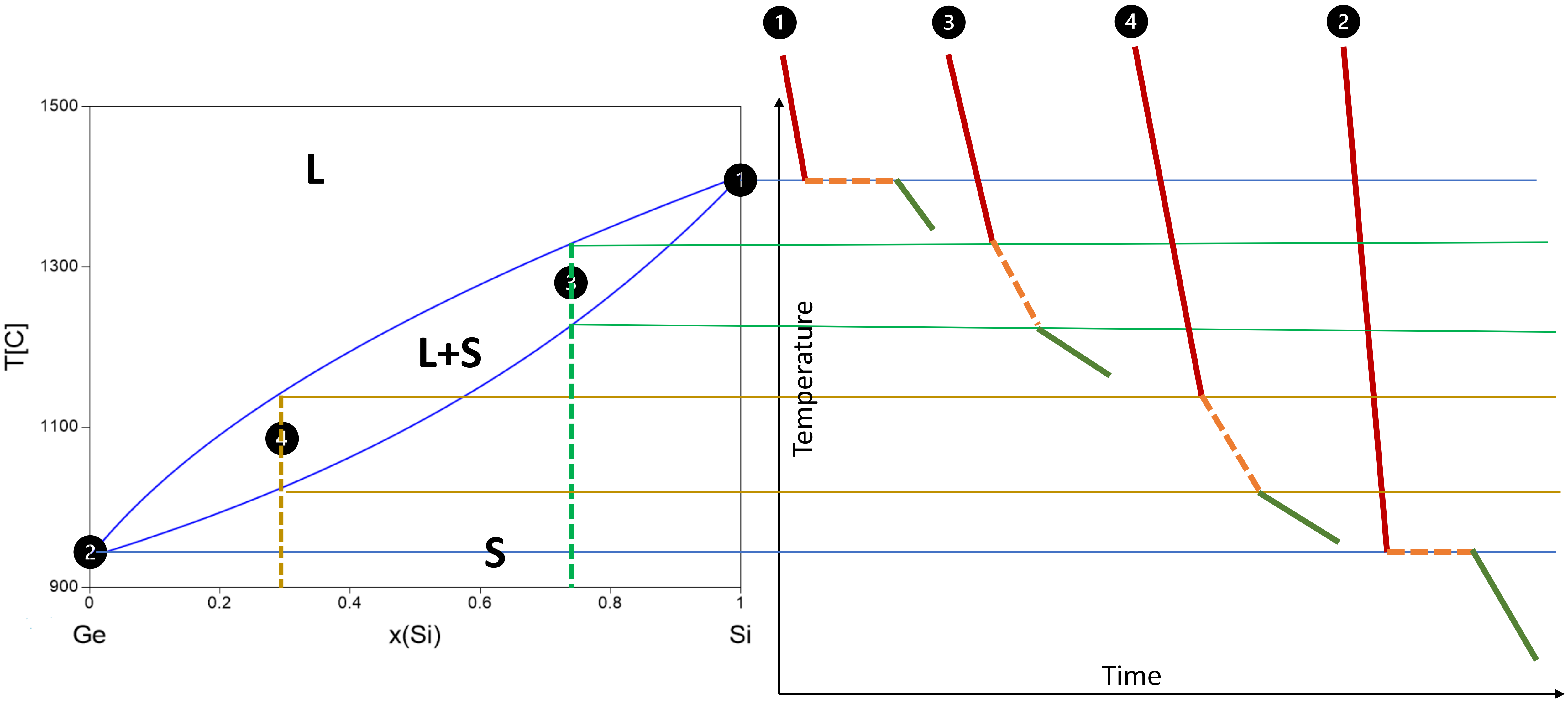
What have we learnt in Lecture-10?

- ❑ Condensed Gibb’s phase rule
- ❑ Tie-line
- ❑ Lever rule

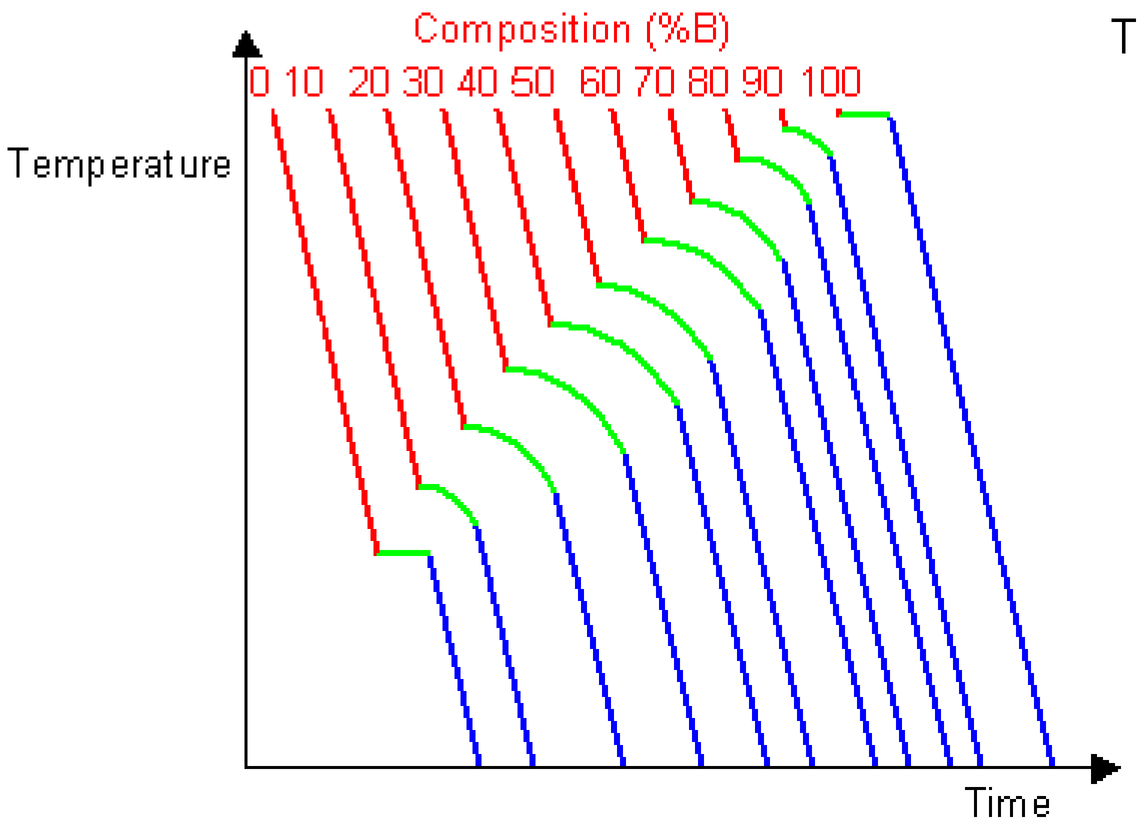
How to construct a phase diagram?

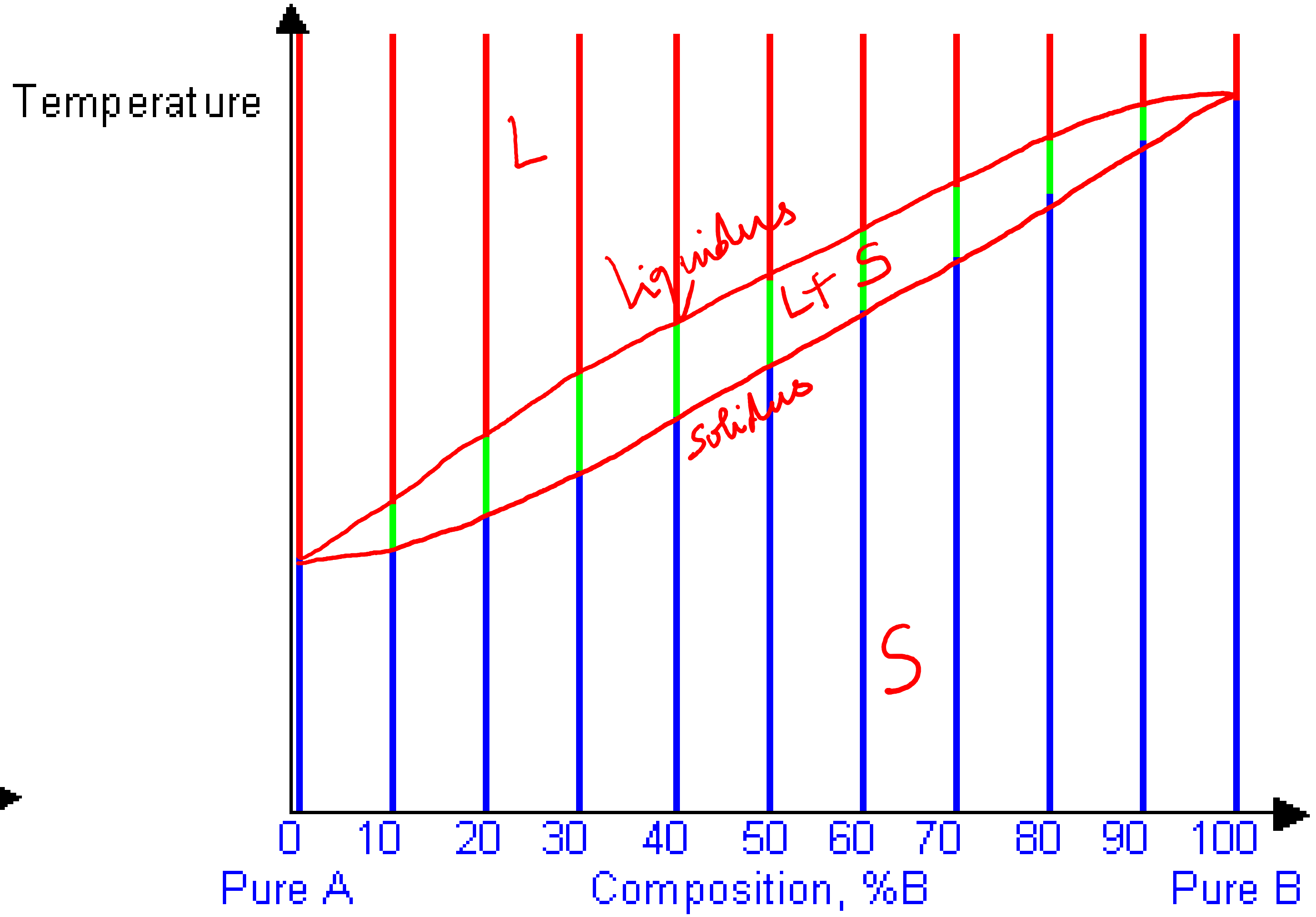
- Determination of phase boundary ---- > liquidus, solidus, solvus, etc.

Cooling curve

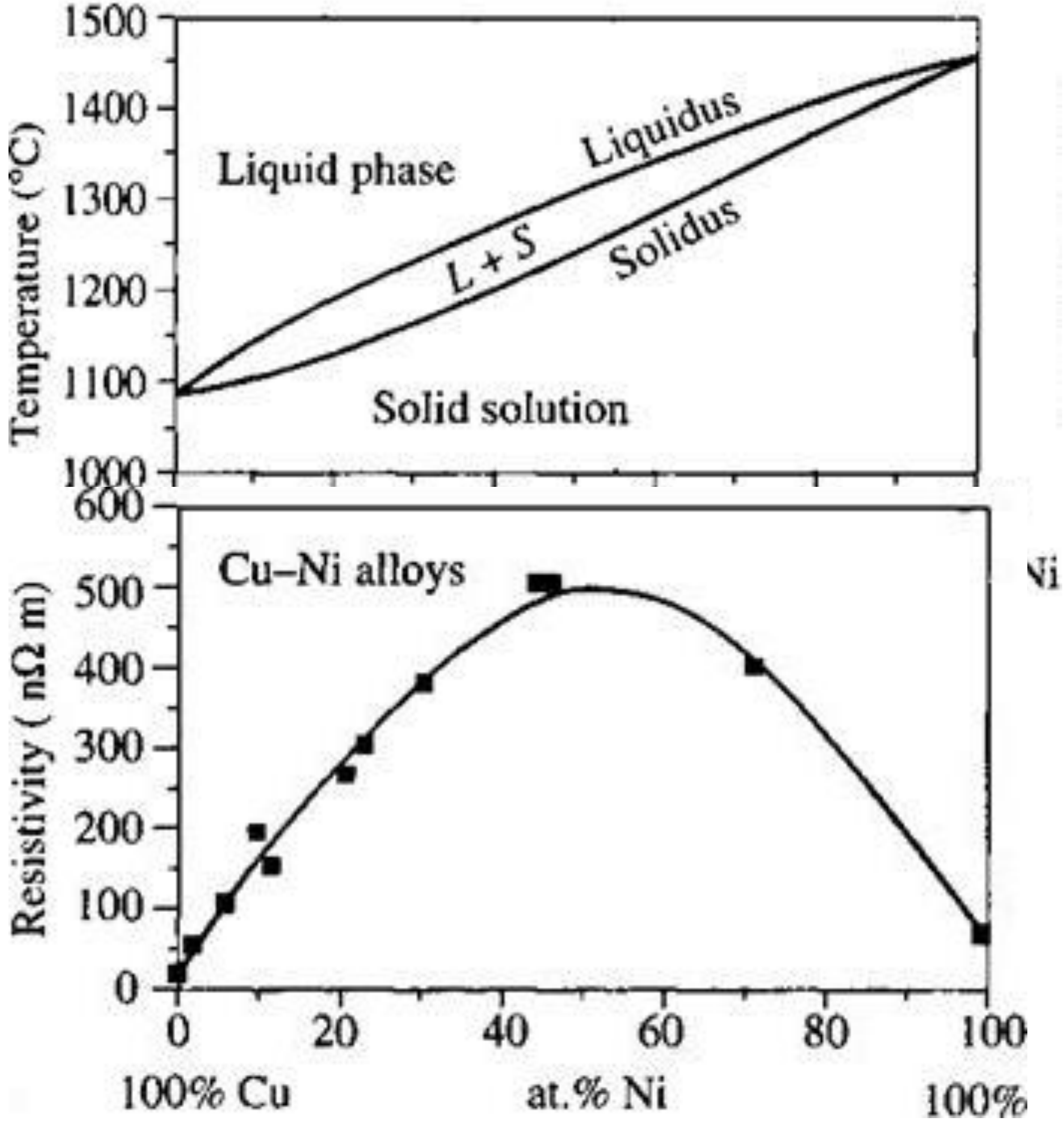


- Pure metals melt at a single temperature (melting point).
- Alloys melt over a range of temperature.


Composition (%B)
0 10 20 30 40 50 60 70 80 90 100
Temperature
Time


Temperature
L
Liquidus
L+S
Solidus
S
0 10 20 30 40 50 60 70 80 90 100
Pure A
Composition, %B
Pure B

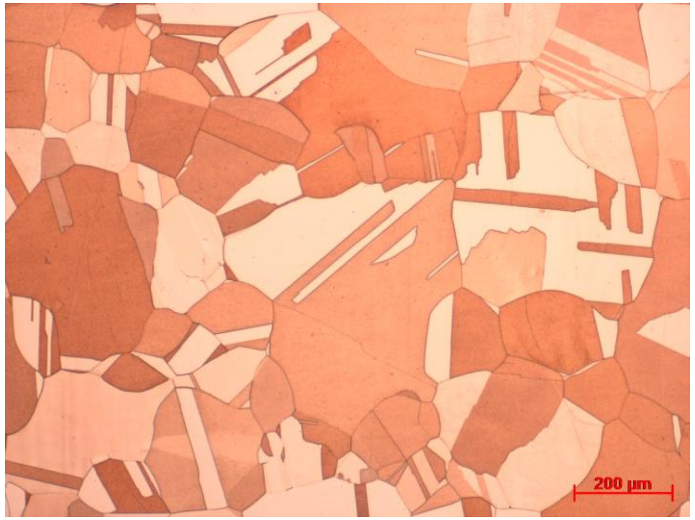
Variation of electrical resistivity of alloys as a function of composition



………. Can you think of any other method using which you may be able to identify the phase boundaries?

Microstructure

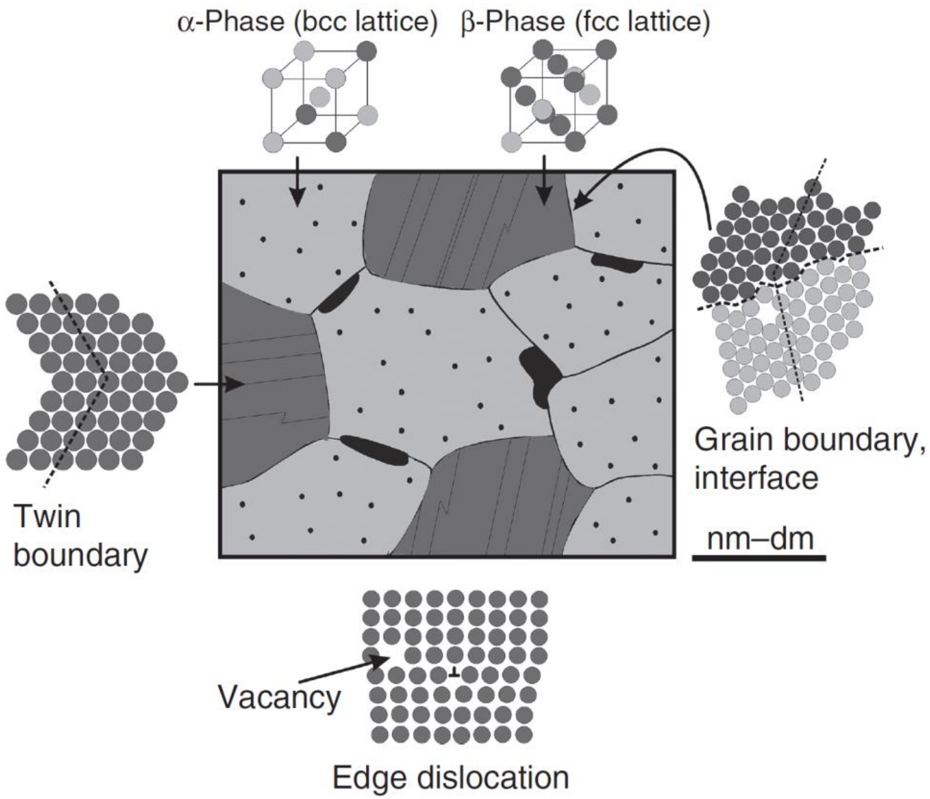


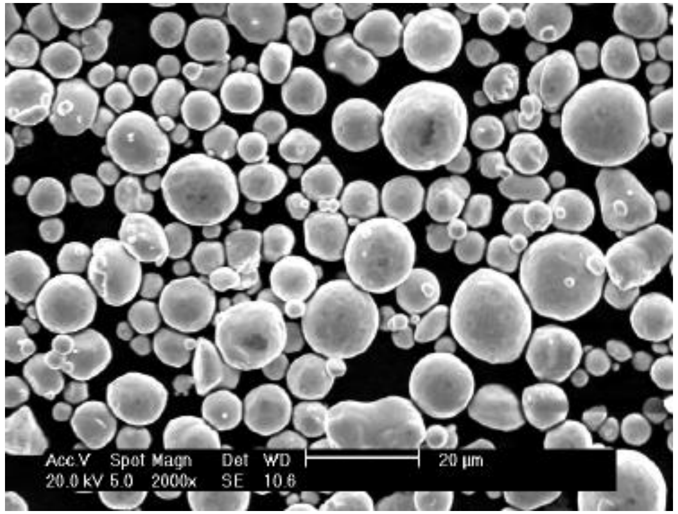



Microstructure obtained through an Optical microscopy

Structural features observed at the micron level in a material

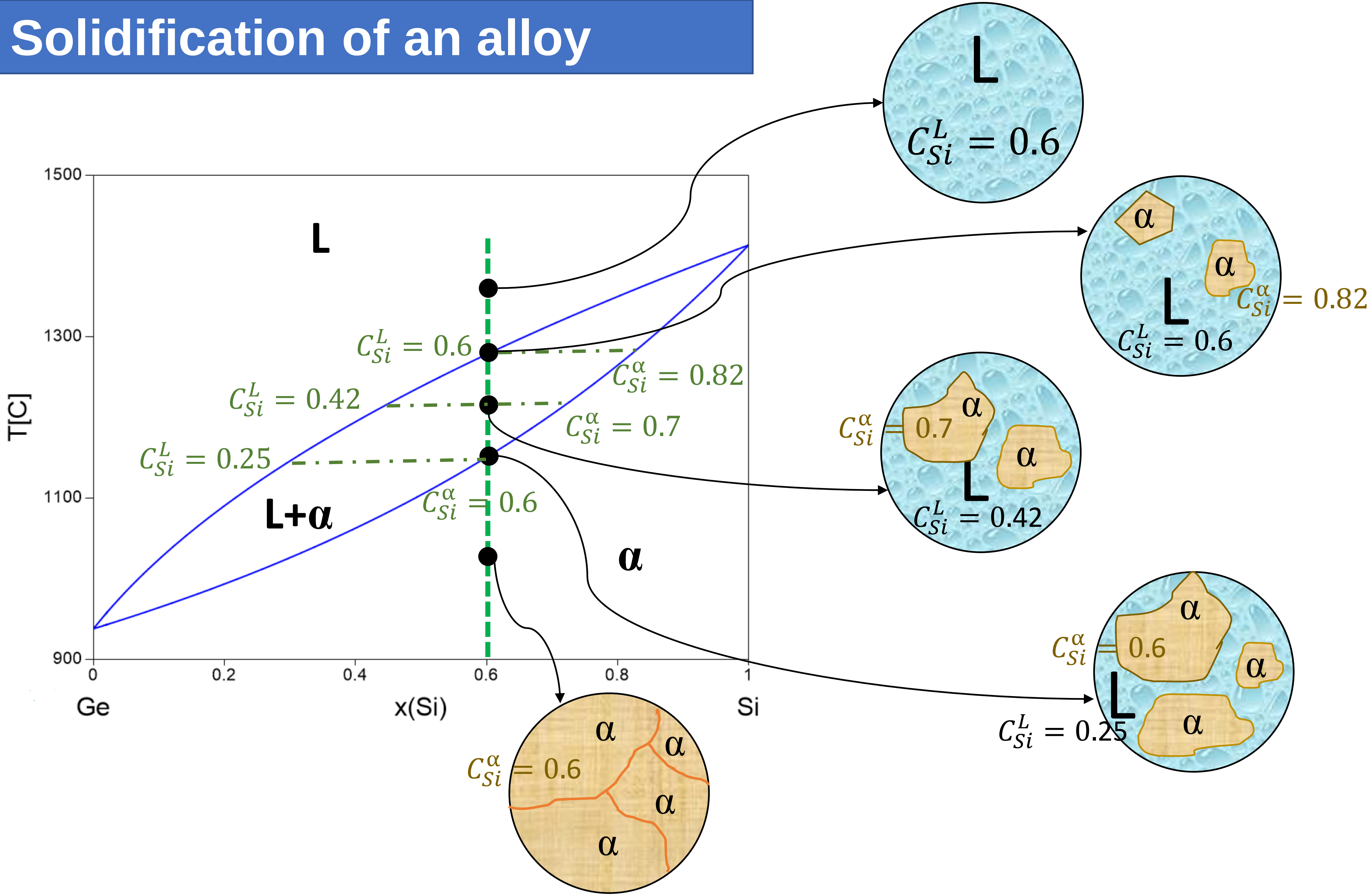
- Phases, Defects, Phase morphology

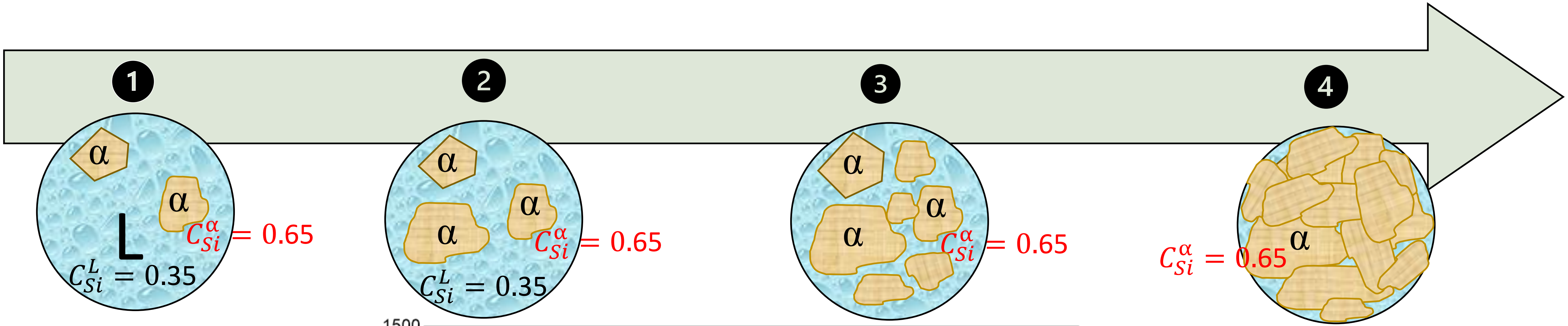


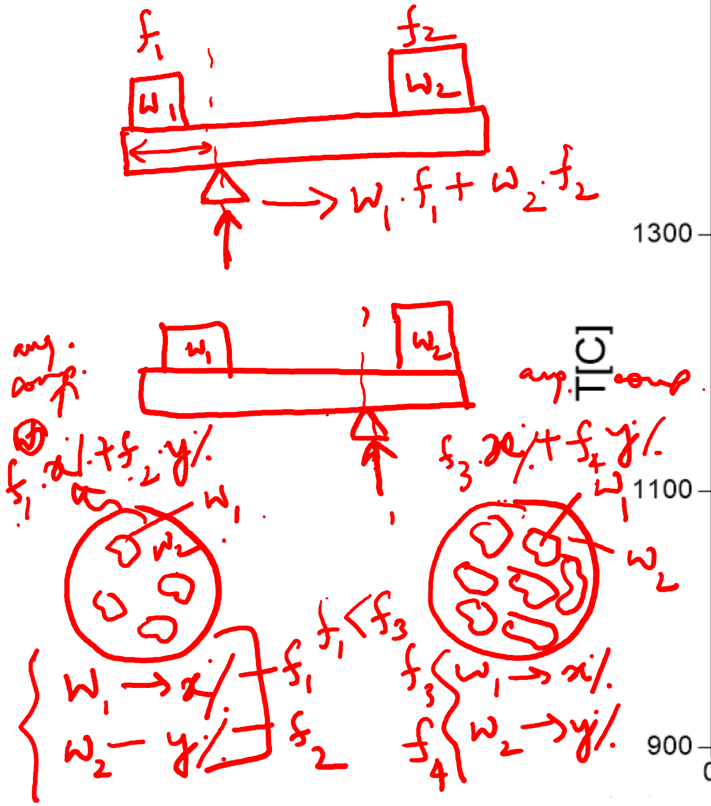


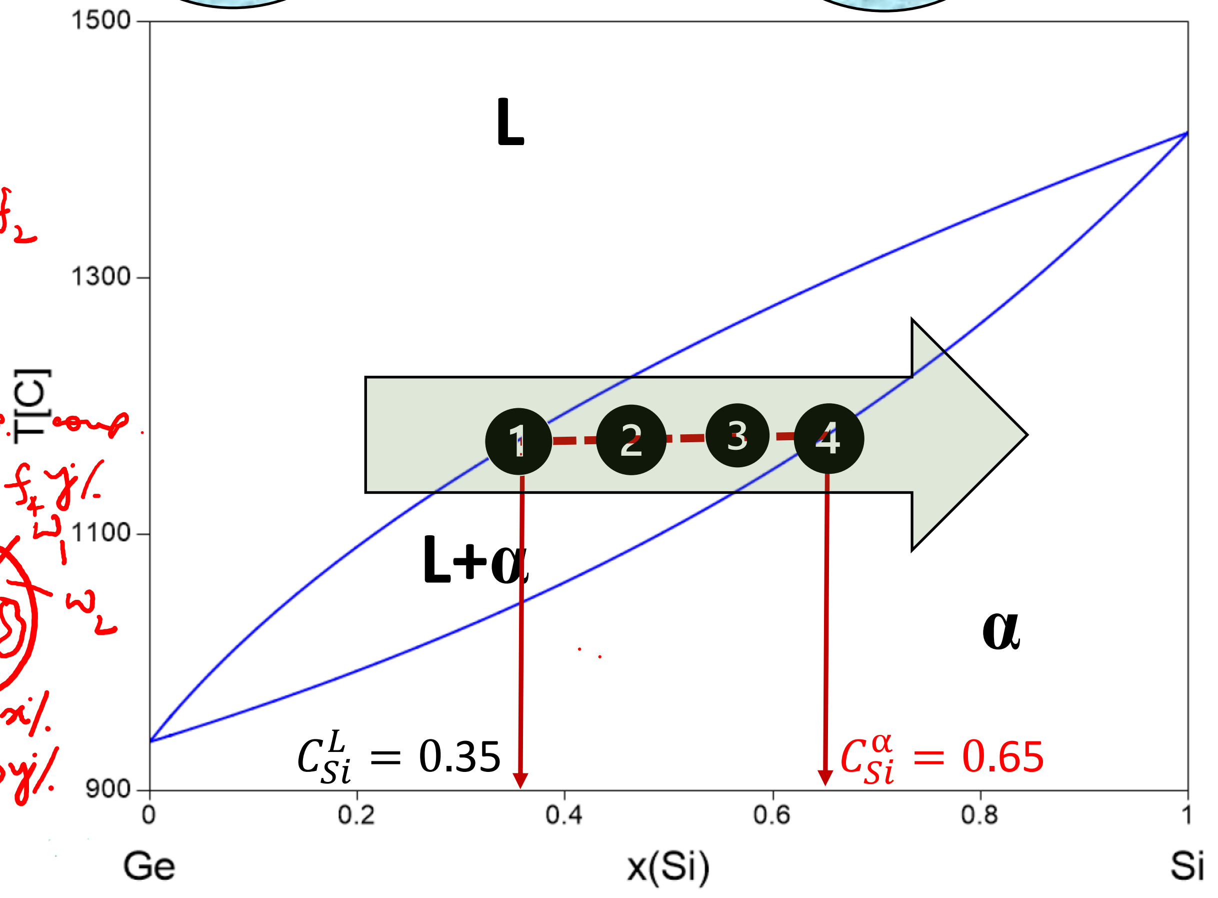
Microstructure obtained through a Scanning Electron Microscopy (SEM)

Solidification of an alloy







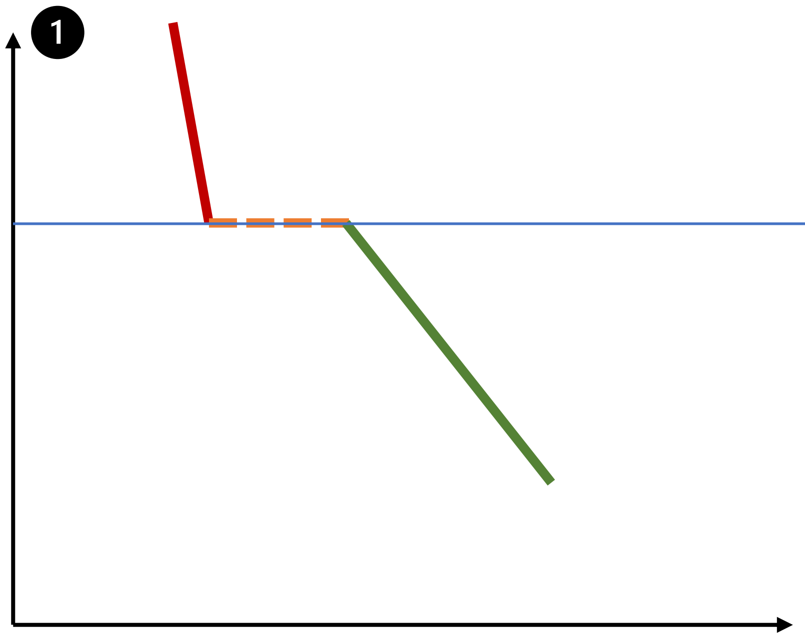


- Alloys along this horizontal line, will consist of two phases, liquid and alpha, whose respective compositions will remain same.
- The difference will be in the fraction of these two phases for different alloys

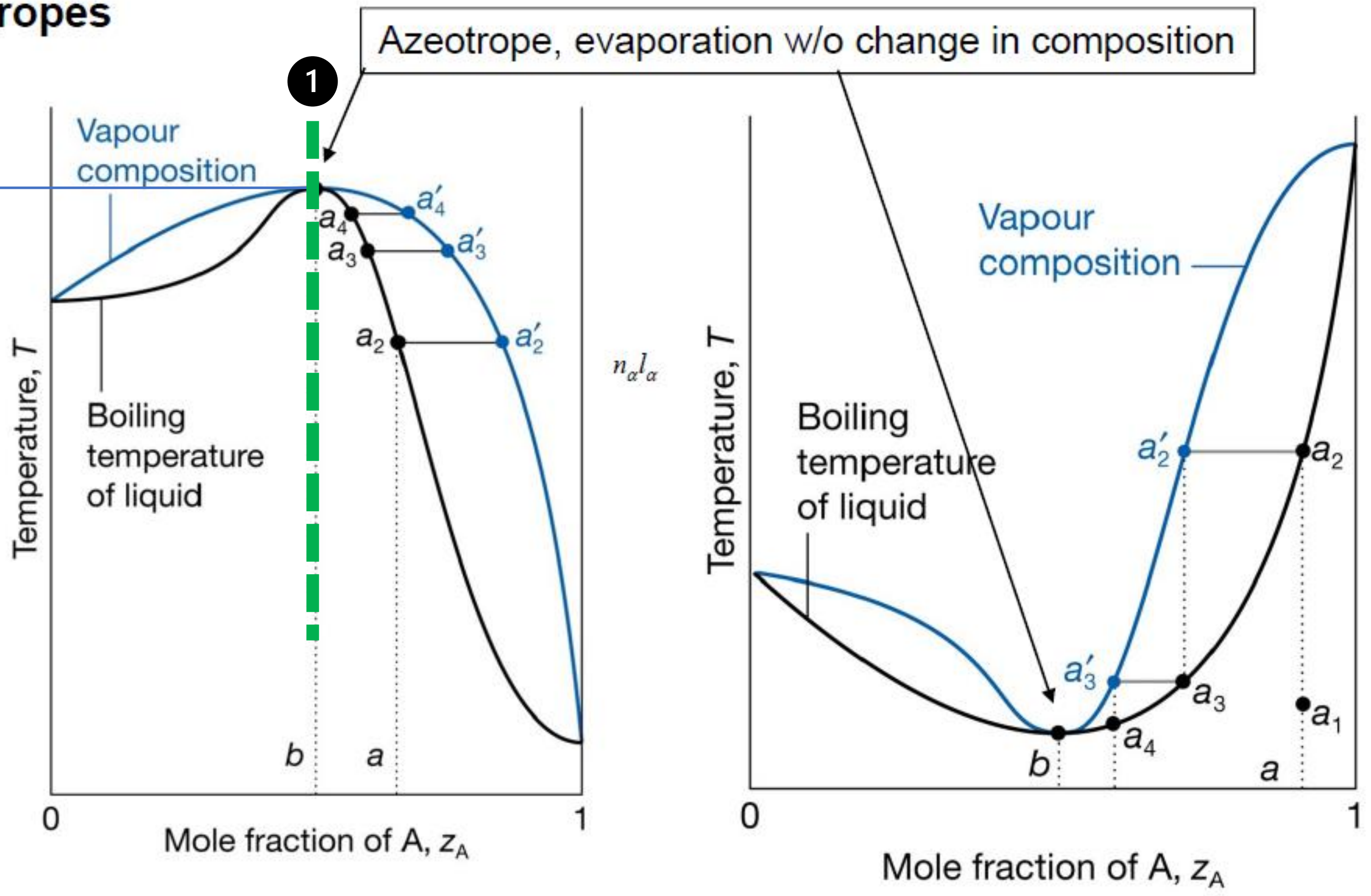
Azeotropes

- Ethanol-water
- Nitric acid-water
- Benzene-water

How will a cooling curve look like for an alloy ‘1’?

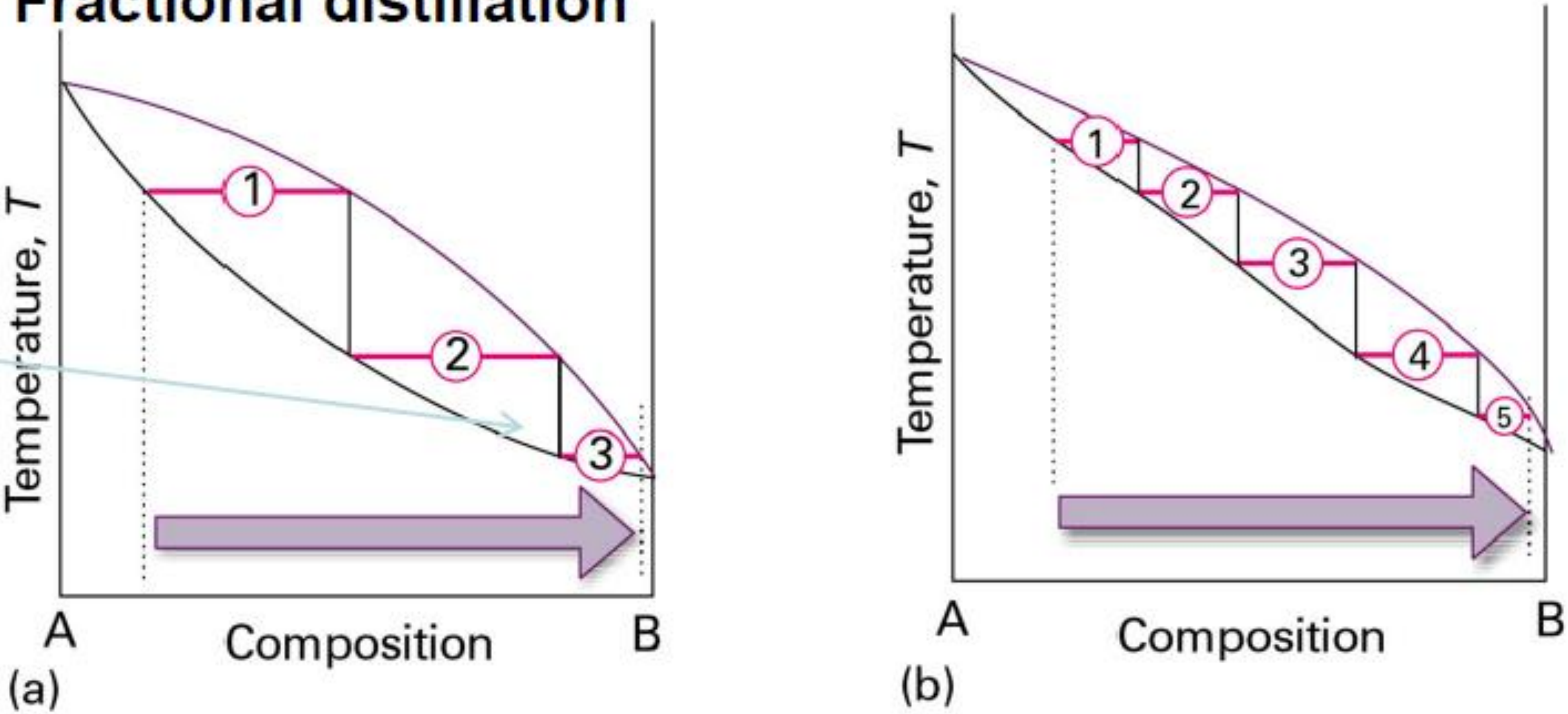


•**Azeotropes**

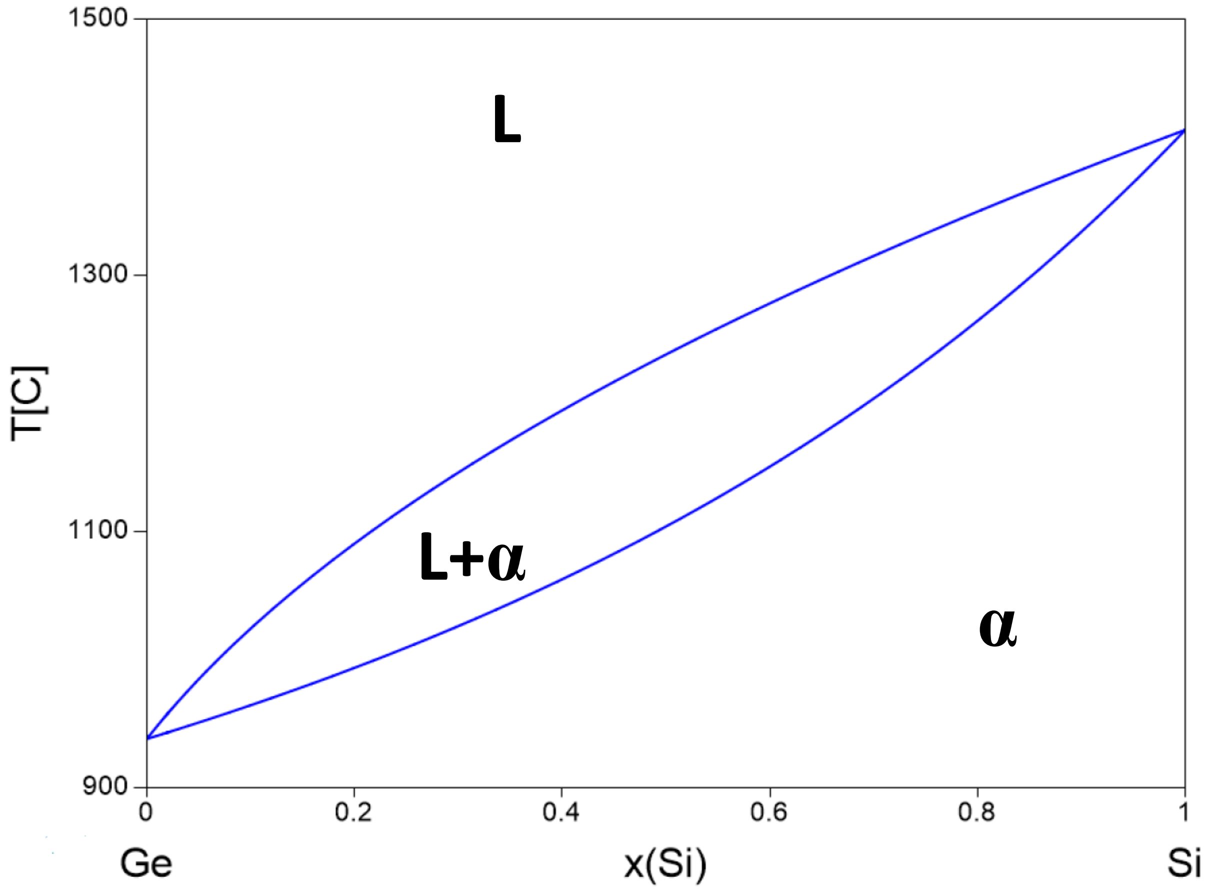


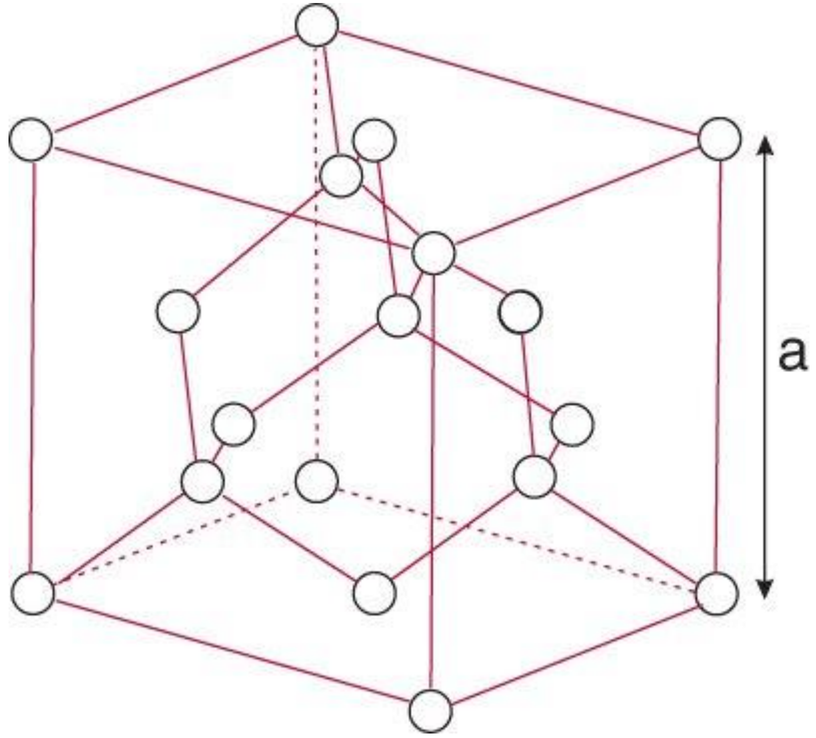
Fractional distillation

number of theoretical plates



Solid solution



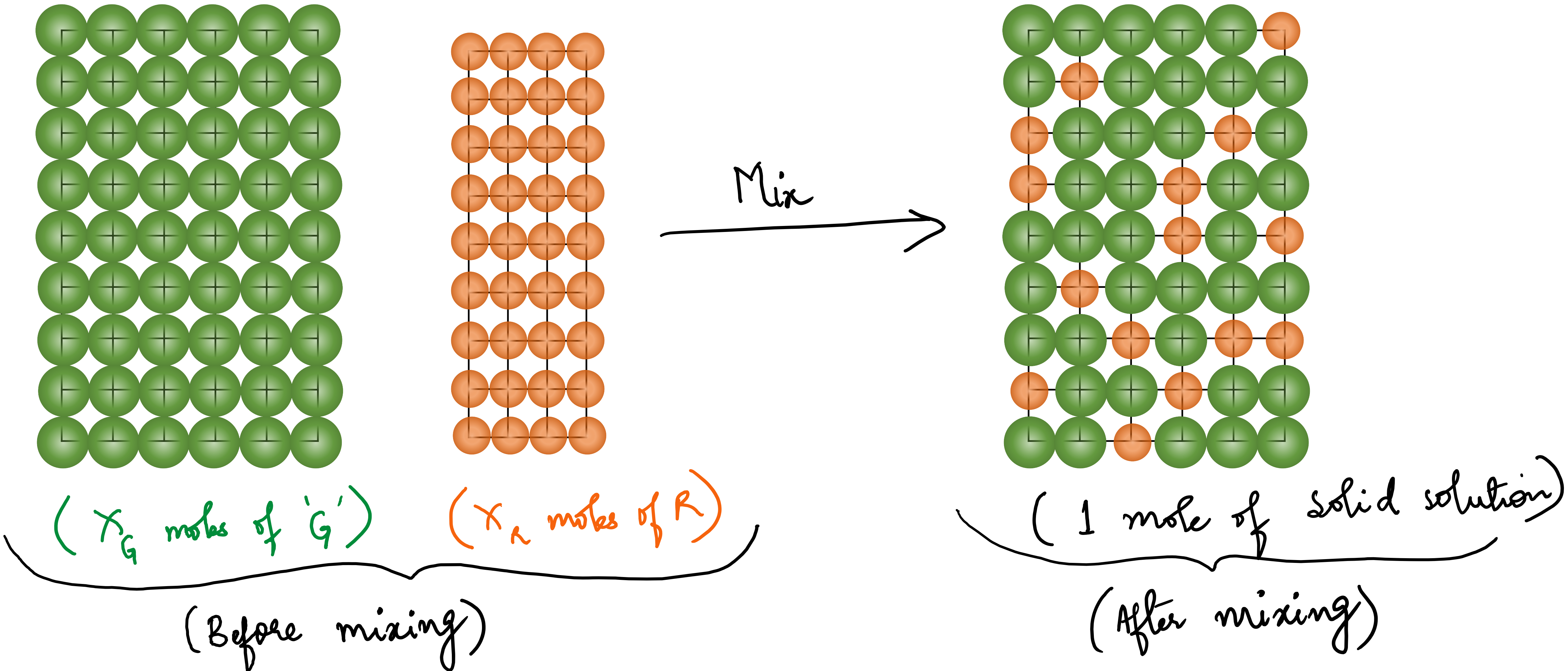


Diamond cubic structure

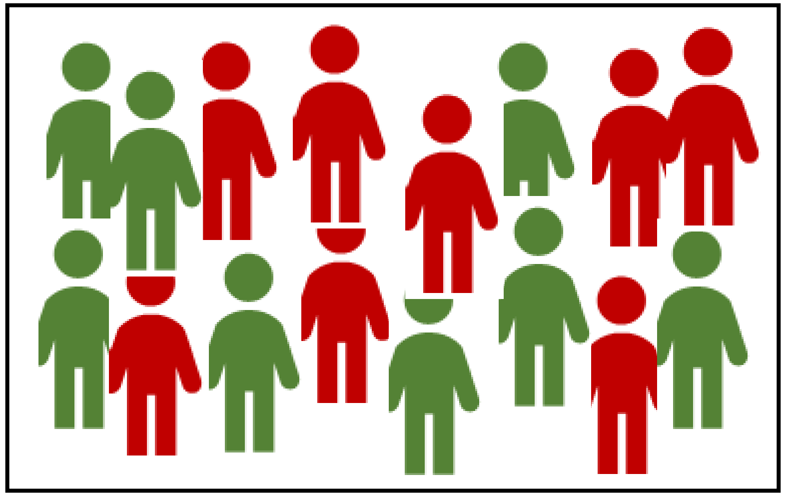
Solid solution

- Consider a system with a total of one mole of atoms
  (X_R and X_G : mole fractions of element R and G respectively)

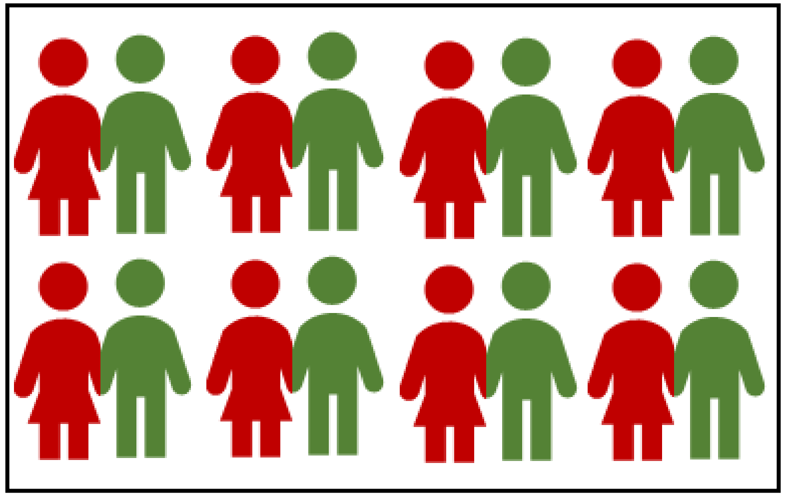
$$X_R + X_G = 1$$



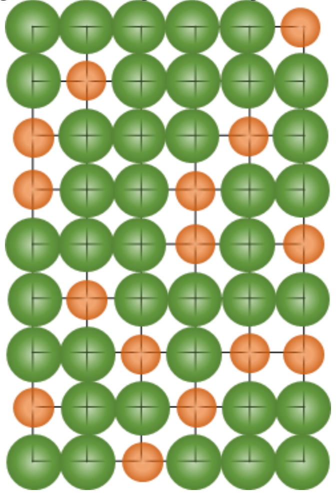
Solid solution (Random configuration): *'R' and 'G' care the least about their environments.*

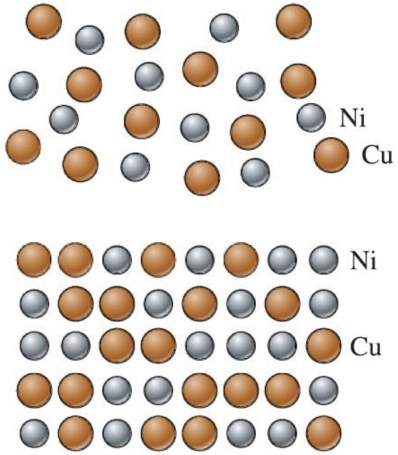


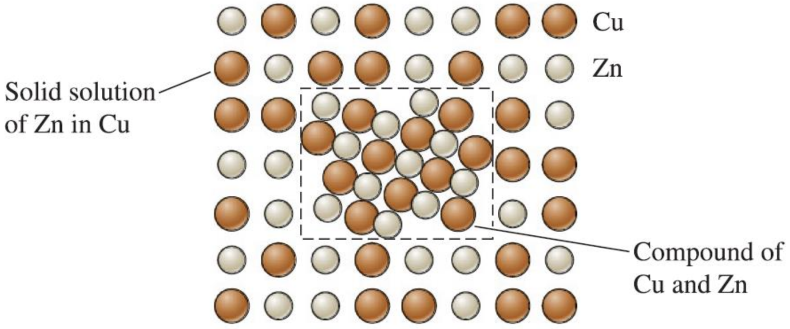
Compound formation (Ordered configuration): *'R' and 'G' feel strongly comfortable in other's space.*



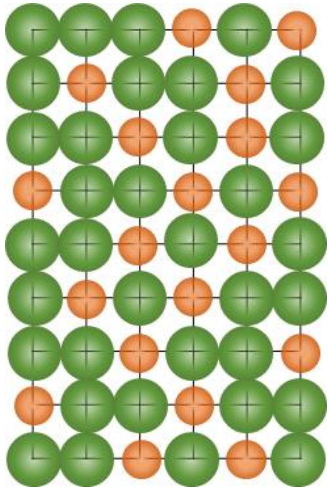
Solid solution (No preference for any bond,







Intermetallic compound (Unlike bonds are preferred)

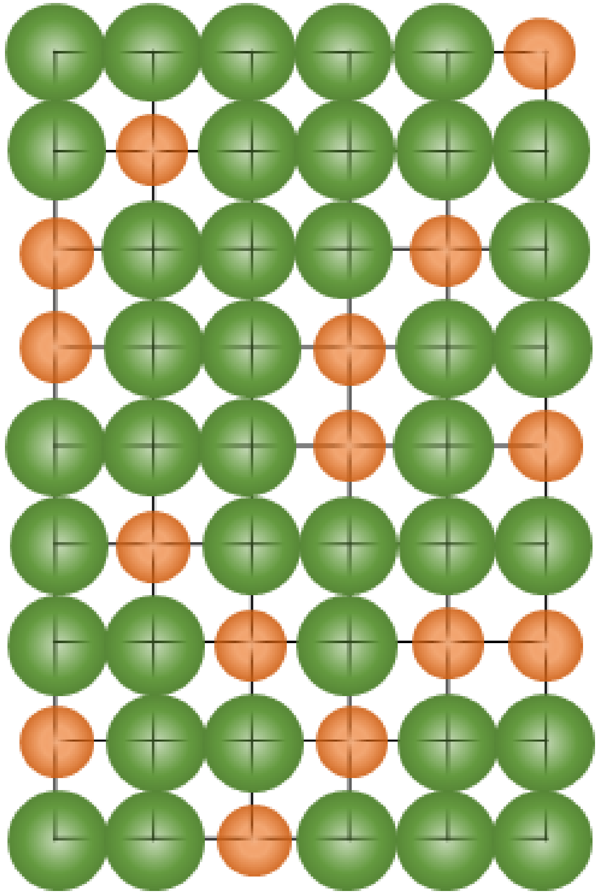


- Variation in composition
- Crystal structure same as that of one of the solid components.

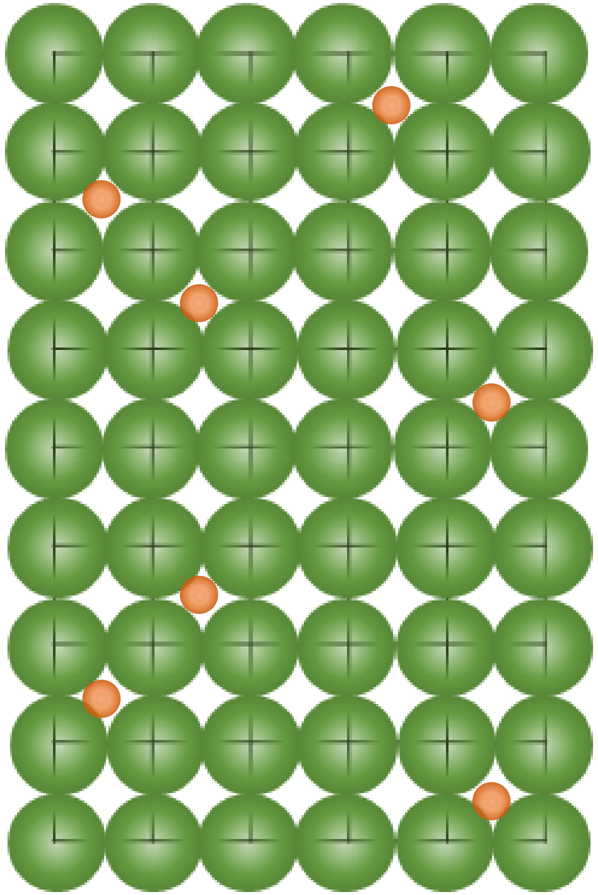
- Fixed composition
- Crystal structure different than those of the solid components.

Types of Solid solution

Substitutional Solid solution



Interstitial Solid solution



Hume Rothery rule

(i) Size factor

When the atomic radii of solute and solvent differ by less than 15%, solid solution is favourable, which otherwise will result in lattice strain.

(ii) Crystal structure

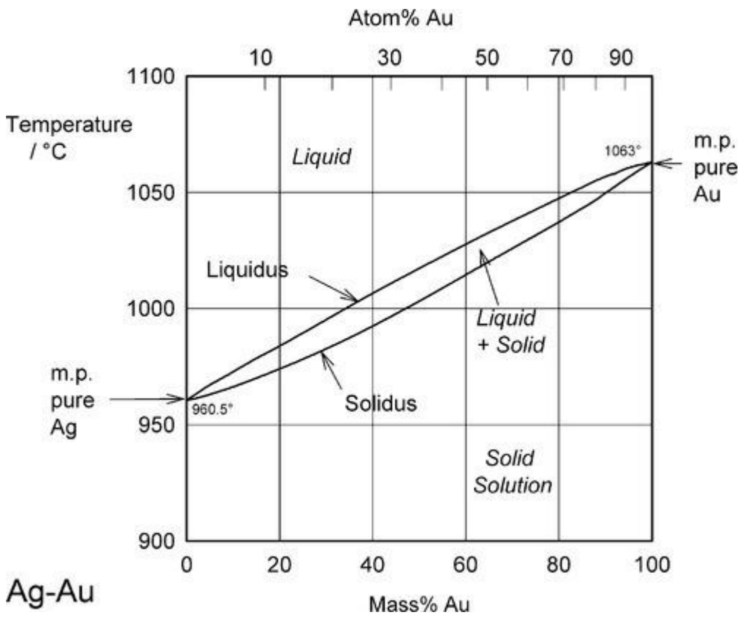
Crystal structures of both the components should be the same.

(iii) Valency

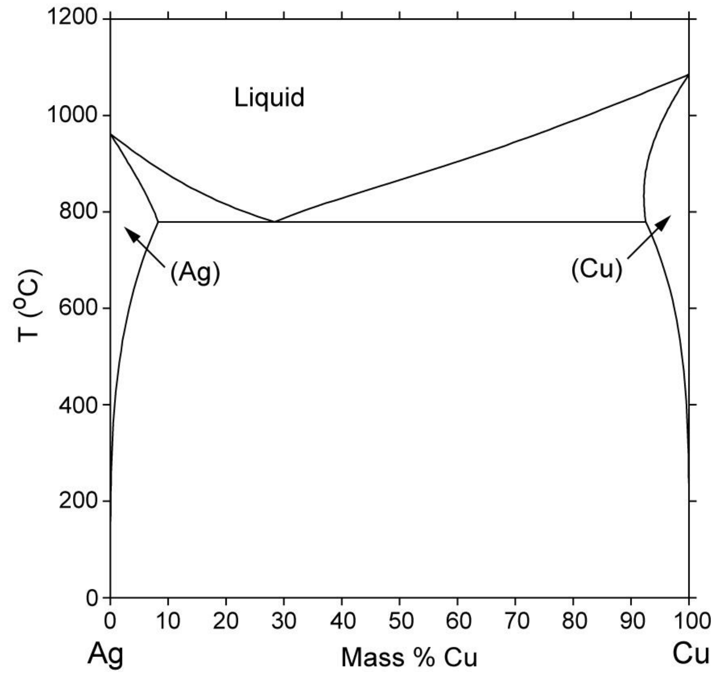
If valency is the same for both the solvent and solute, then a complete miscibility is possible.
Solubility is higher when the solvent has a higher valence.

(iv) Electronegativity

Similar electronegativity favours a higher solubility. The higher the difference, the greater the possibility for the formation of new compound phase.



Elements	Atomic size	Electronegativity	Crystal structure	Valency
Cu	140 pm	1.9	FCC	+2
Ni	149 pm	1.91	FCC	+2
	$\Delta AS = 6\%$			



Cu	140 pm	1.9	FCC	+2
Ag	165 pm	1.93	FCC	+1
	$\Delta AS = 18\%$			

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Introduction to Materials Science and Engineering

Lecture-12 (February 01, 2022)

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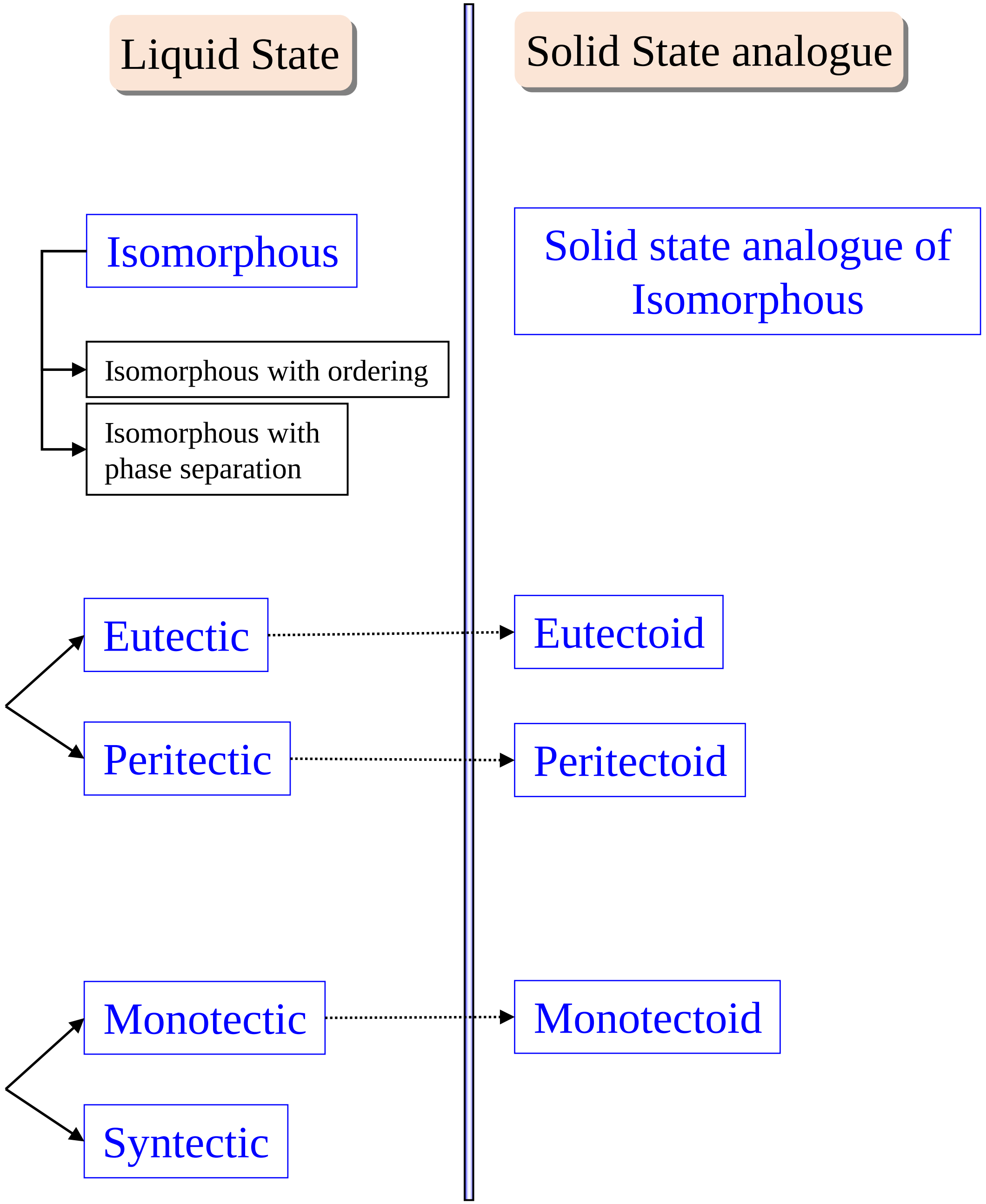
Department of Materials Science and Engineering

What have we learnt in Lecture-11?

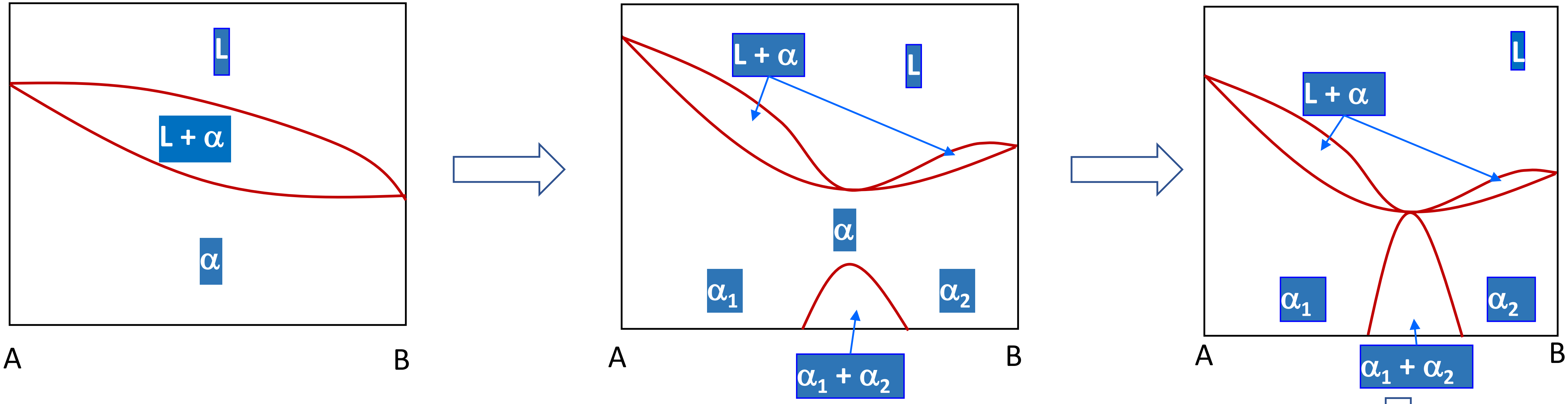
- Cooling curve
- Microstructure
- Solidification of an alloy in an isomorphous system
- Solid solution
- Hume Rothery rule

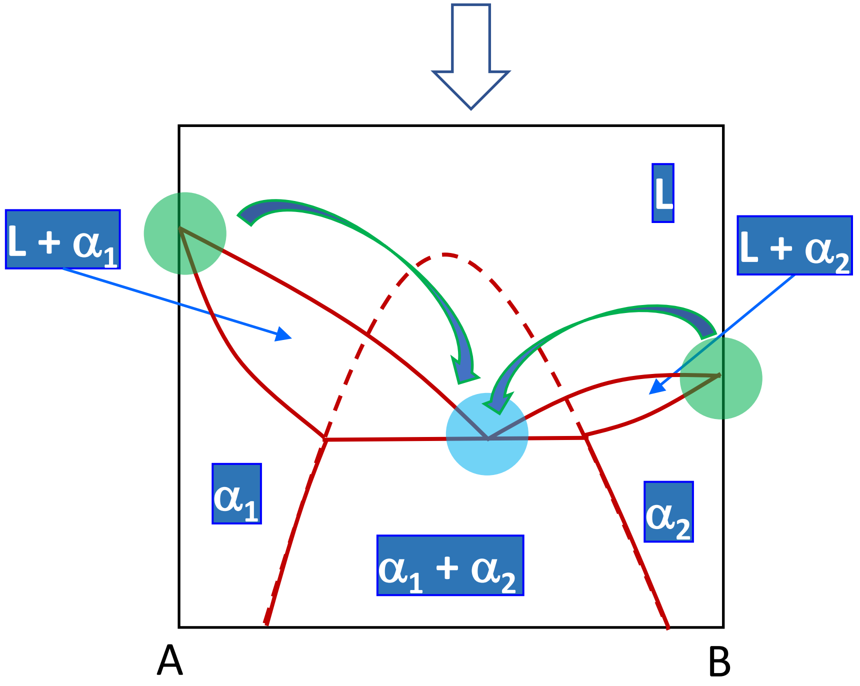
Possible scenarios in a binary phase diagram



- **Complete solubility in both liquid and solid states**
- **Complete Solubility in liquid state, but limited solubility in the solid state**
- **Limited Solubility in both liquid and solid states**

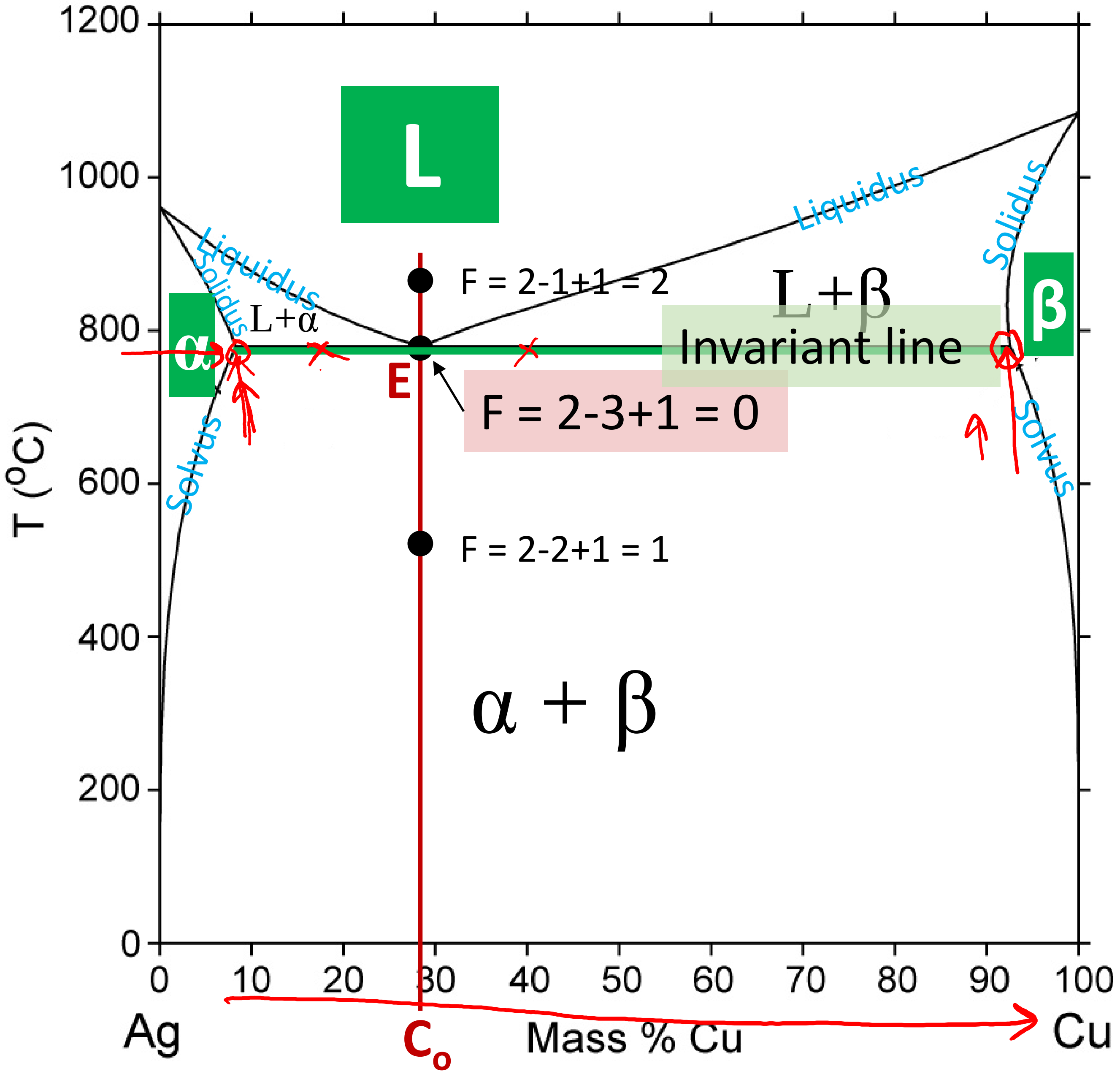
Isomorphous ⟶ Eutectic phase diagram





- *Eutēktos: Easily melted*
- Any homogeneous material melting or solidifying at a particular temperature which is lower than the melting point of any of the components.

Eutectic phase diagram



Invariant point

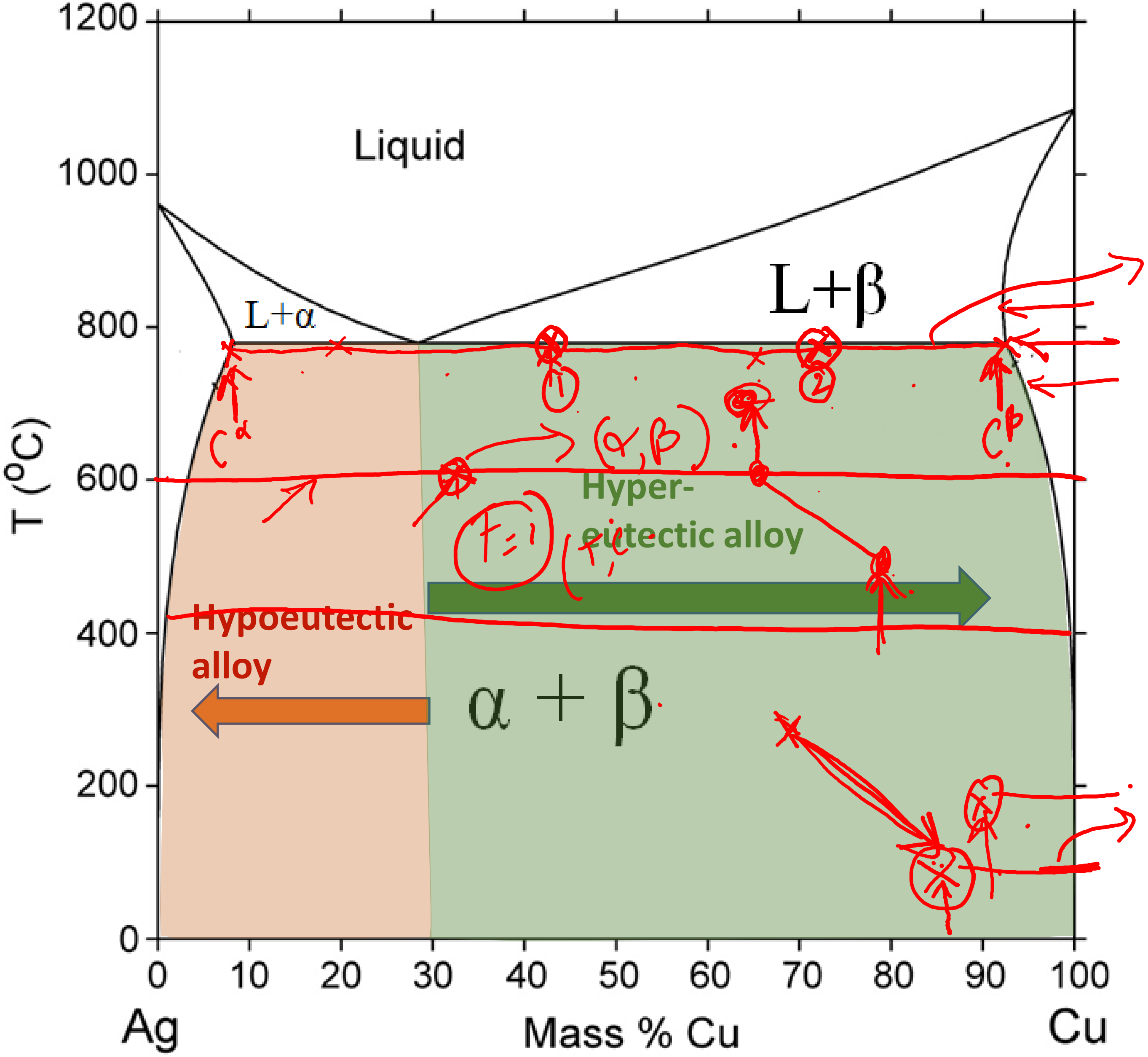
Invariant: Remains unchanged

- *Eutectic point* ('E') is an invariant point which occurs at a fixed composition and temperature for a given binary phase diagram.
- At 'E', eutectic reaction takes place:

$$L(C_o) \xrightarrow{\text{cooling}} \alpha + \beta$$

- Green line is the invariant line.
- **Solvus phase boundary**: Boundary line that divides a solid solution and a two-phase solid solution region.

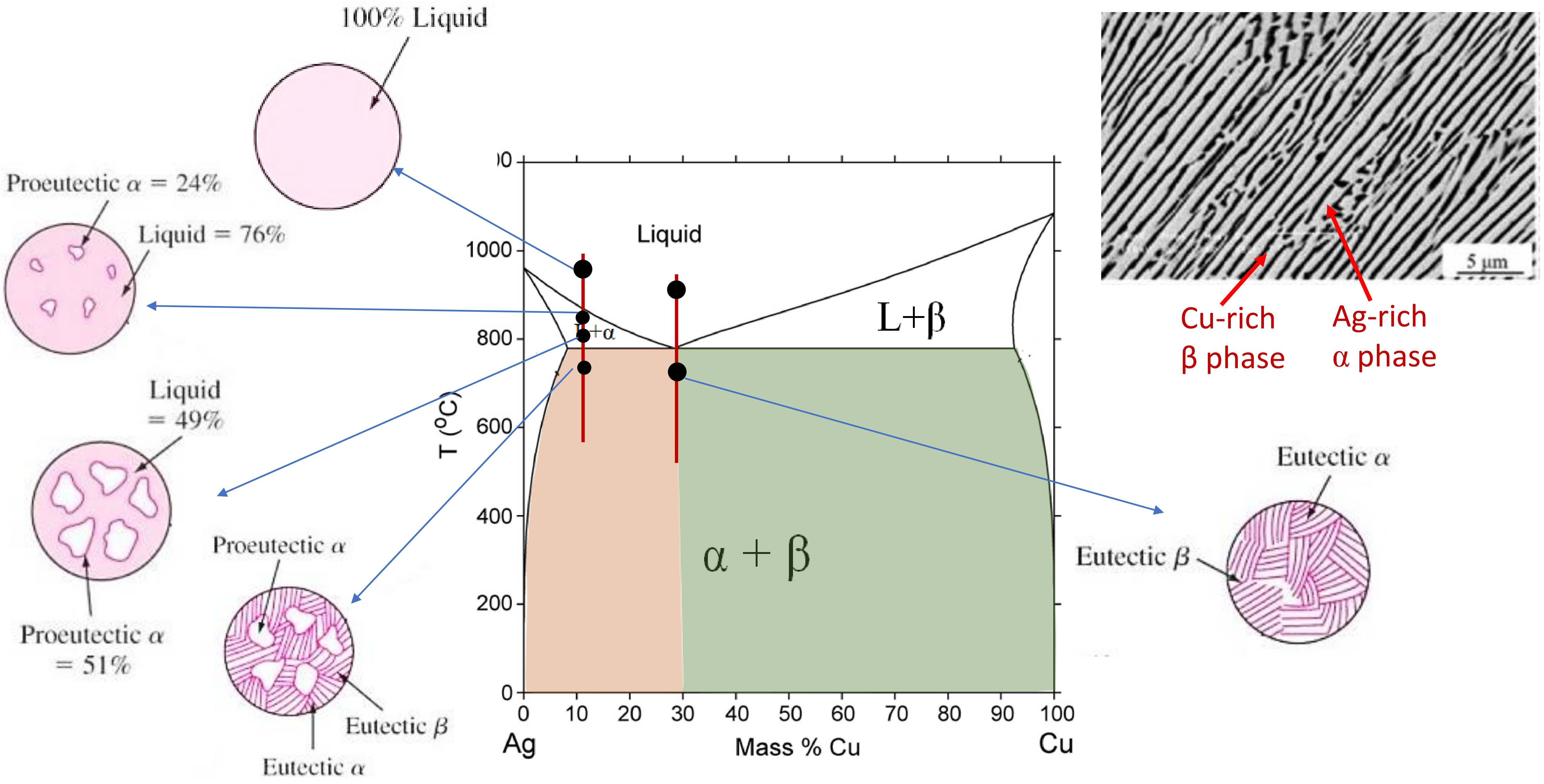
Hypo- and Hyper-eutectic alloy



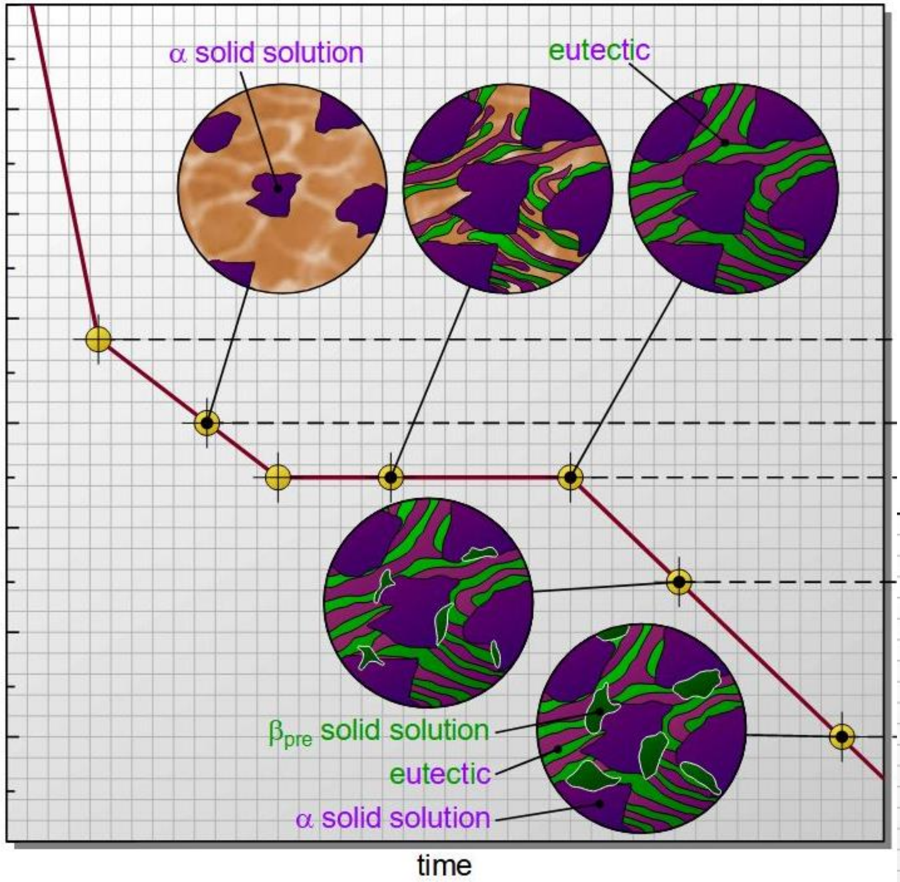
Eutectic line (T is fixed)

(C^{α}, C^{β}) → ①, ②

Microstructural evolution of hypoeutectic alloy and eutectic alloy

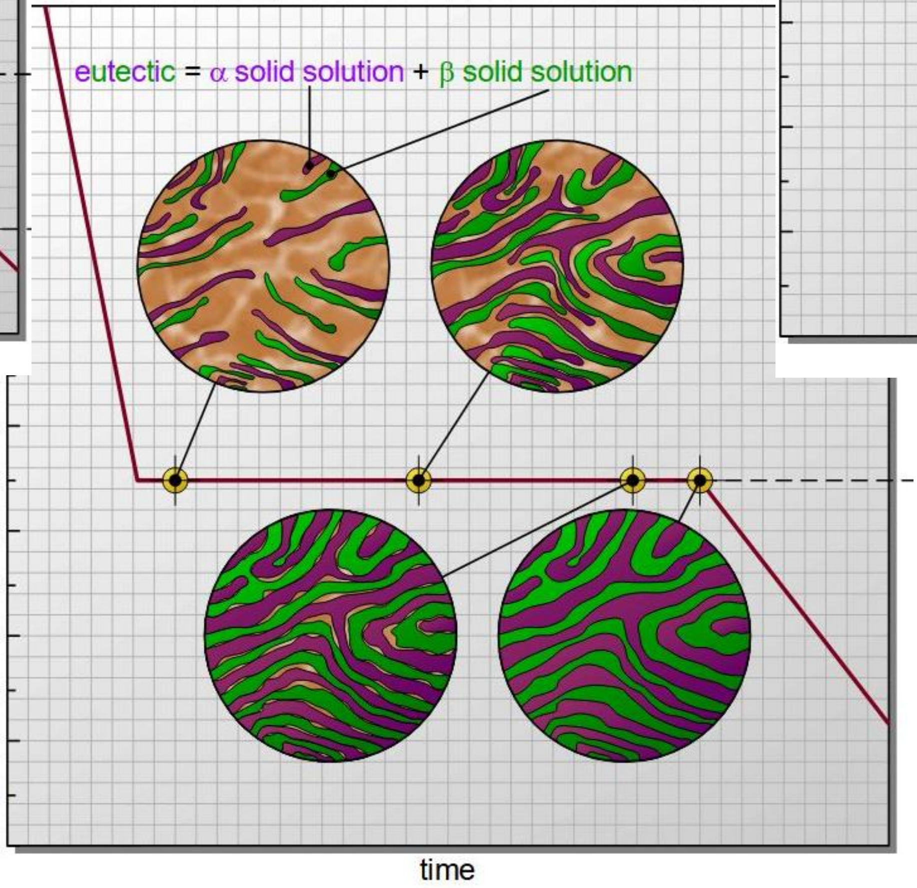


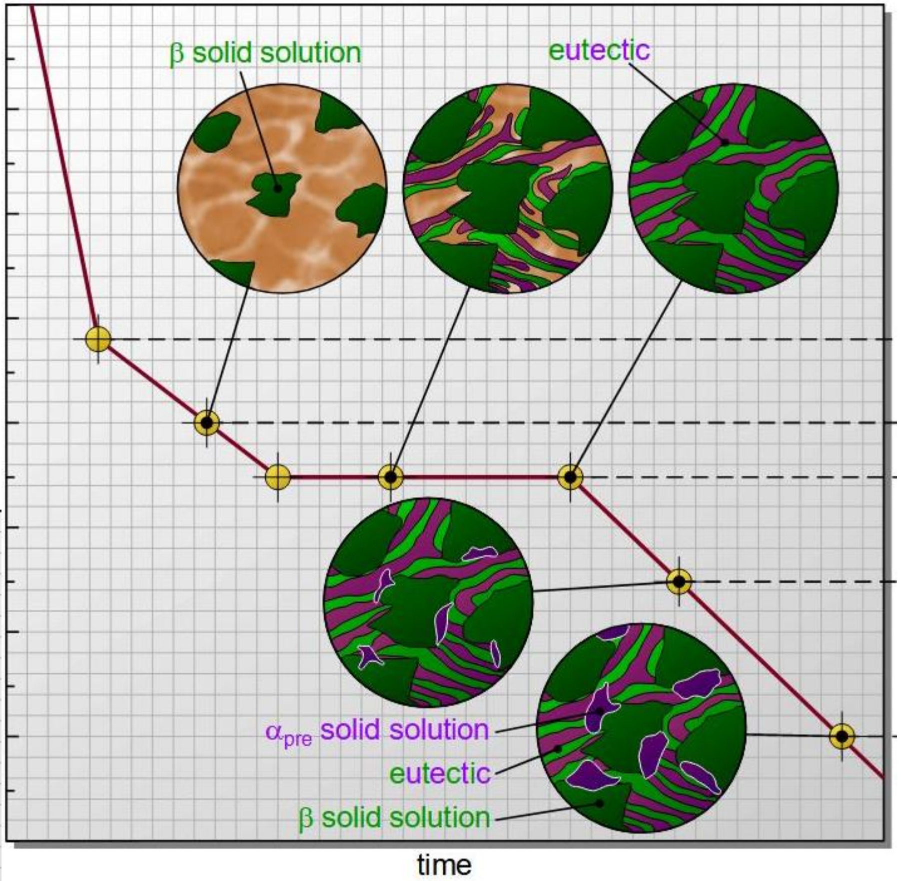
Cooling curve



Solidification of a hypoeutectic alloy

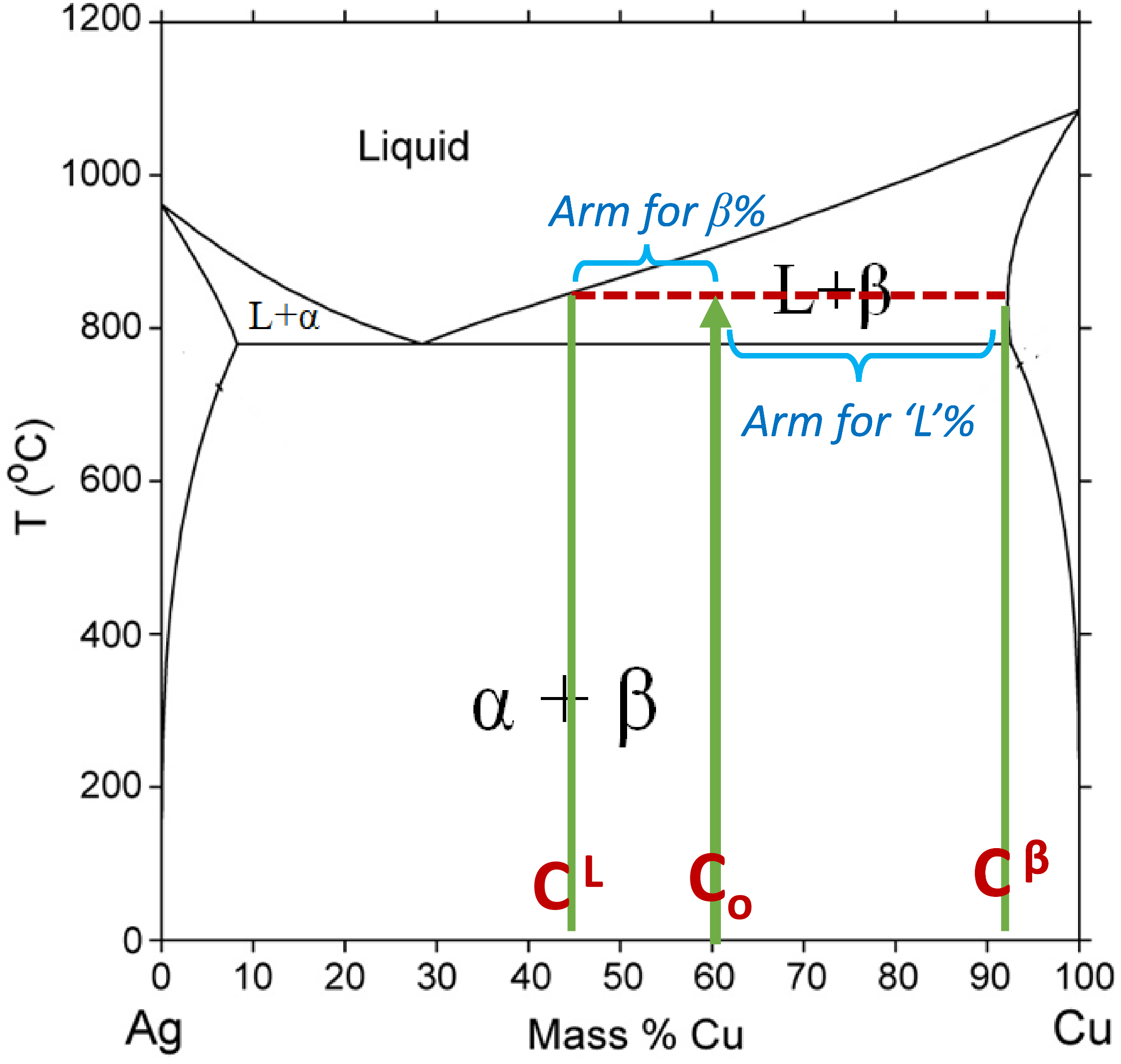
Solidification of an eutectic alloy





Solidification of a hypereutectic alloy

What are the fractions of 'L' and 'β' phases present at T = 830 °C for an alloy with composition of C_o?



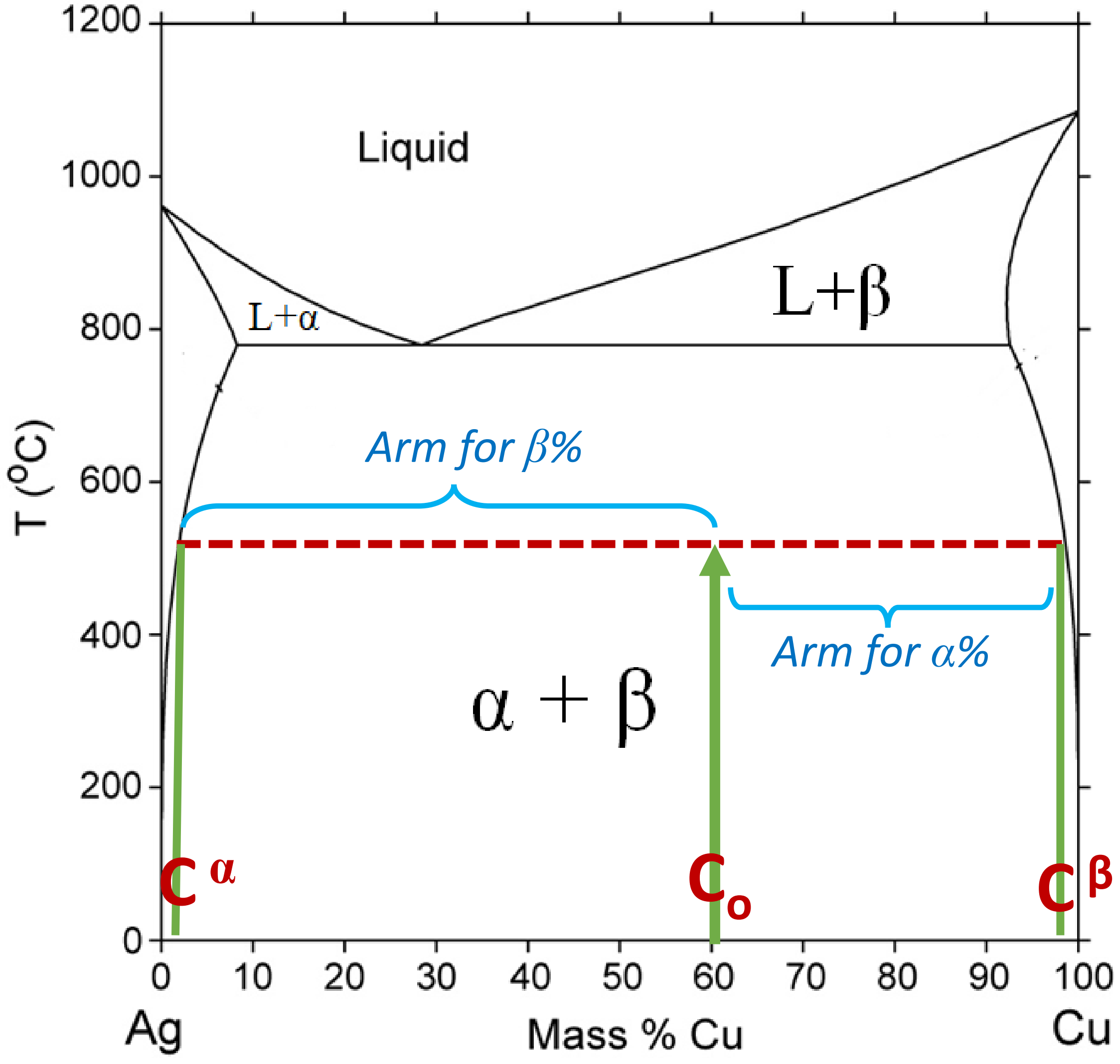
$$f_\beta = \frac{(C_o - C^L)}{(C^\beta - C^L)}$$

$$f_\beta = \frac{(60 - 45)}{(92 - 45)}$$

$$f_\beta = 32\%$$

$$f_L = 68\%$$

What are the fractions of 'α' and 'β' phases present at T = 530 °C for an alloy with composition of C_o?



$$f_\beta = \frac{(C_o - C^\alpha)}{(C^\beta - C^\alpha)}$$

$$f_\beta = \frac{(60-2)}{(98-2)}$$

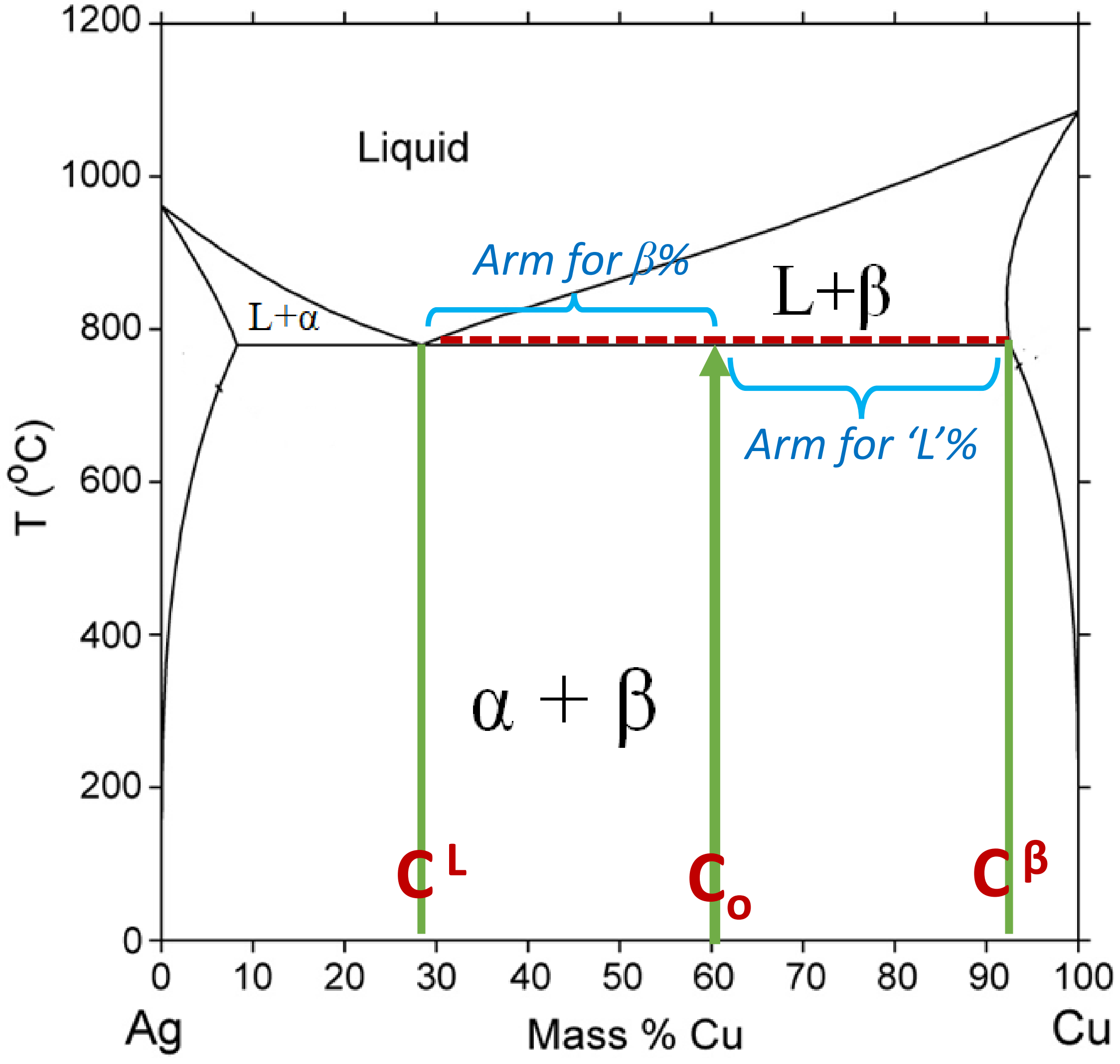
$$f_\beta = 60.4\%$$

$$f_\alpha = \frac{(C^\beta - C_o)}{(C^\beta - C^\alpha)}$$

$$f_\alpha = \frac{(98-60)}{(98-2)}$$

$$f_\alpha = 39.6\%$$

What are the fractions of 'L' and 'pro-eutectic β' phases present at the eutectic temperature for an alloy with composition of C_o?



$$f_\beta = \frac{(C_o - C^L)}{(C^\beta - C^L)}$$

$$f_\beta = \frac{(60 - 28)}{(92 - 28)}$$

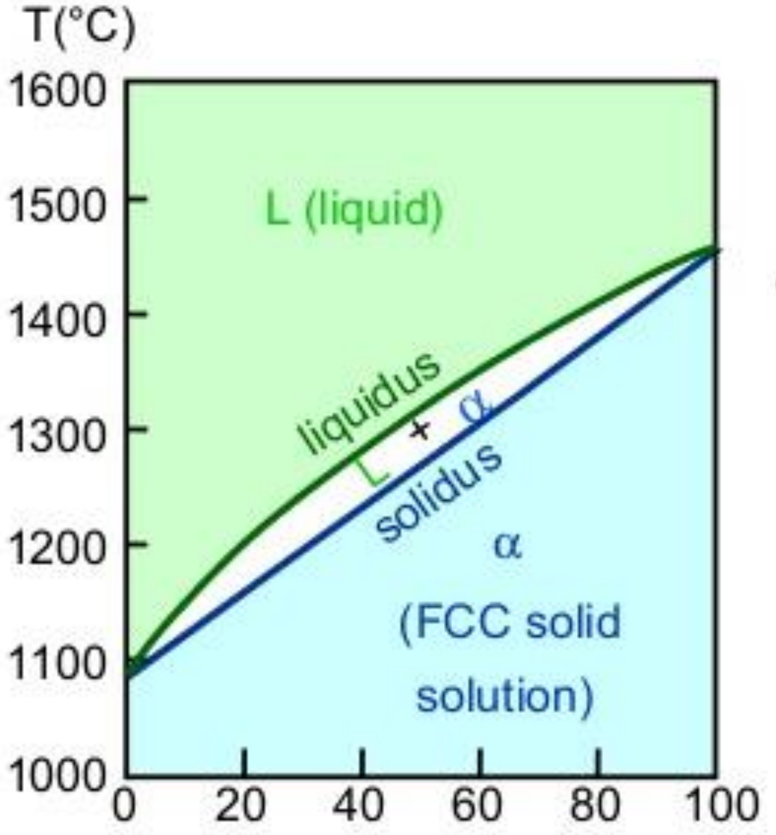
$$f_\beta = 50\%$$

$$f_L = \frac{(C^\beta - C_o)}{(C^\beta - C^L)}$$

$$f_L = \frac{(92 - 60)}{(92 - 28)}$$

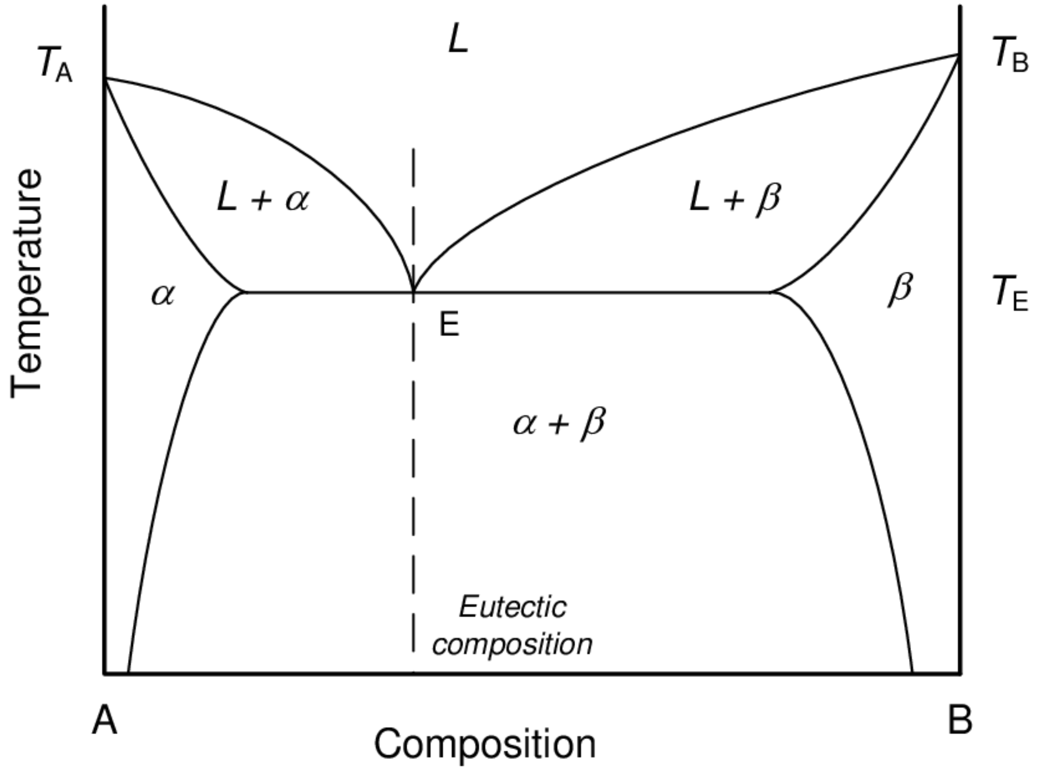
$$f_L = 50\%$$

Isomorphous

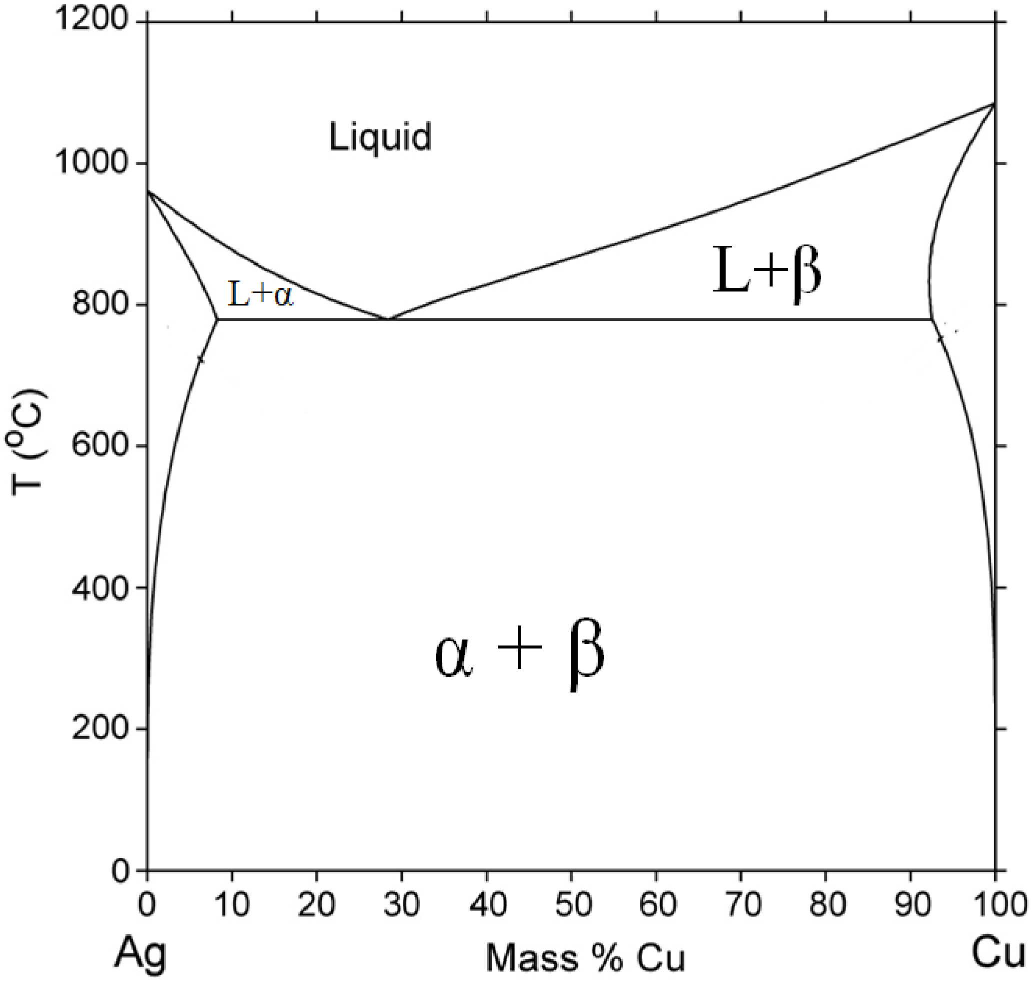


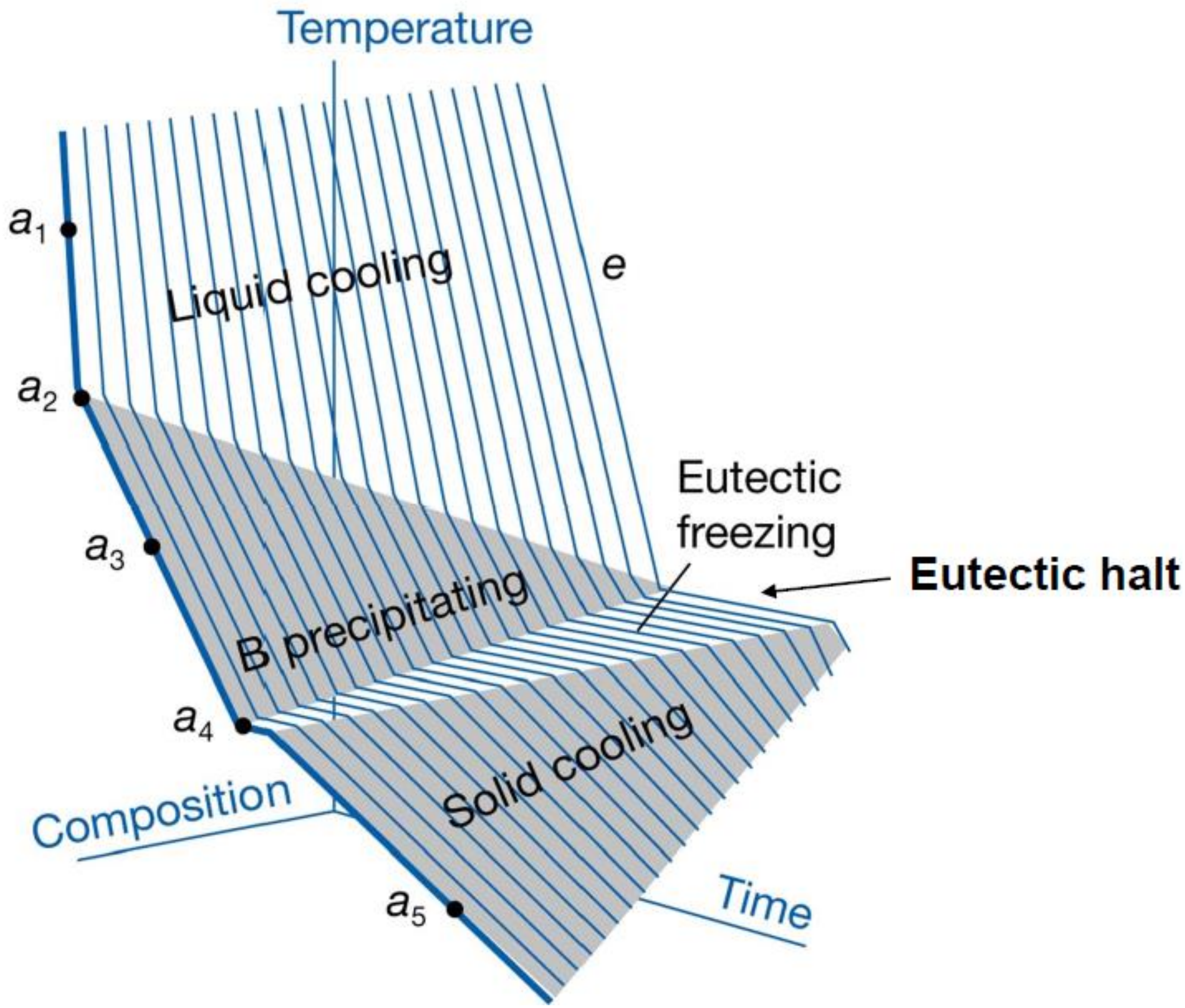
$$L \xrightarrow{\text{cooling}} S$$

Eutectic



$$L \xrightarrow{\text{cooling}} S_1 + S_2$$


1200
1000
800
600
400
200
0
T (°C)
Liquid
L+α
L+β
α + β
0
10
20
30
40
50
60
70
80
90
100
Ag
Mass % Cu
Cu


Temperature
a_1
a_2
a_3
a_4
a_5
Liquid cooling
e
Eutectic
freezing
Eutectic halt
B precipitating
Solid cooling
Composition
Time

MLL 100

Introduction to Materials Science and Engineering

Lecture-13 (February 02, 2022)

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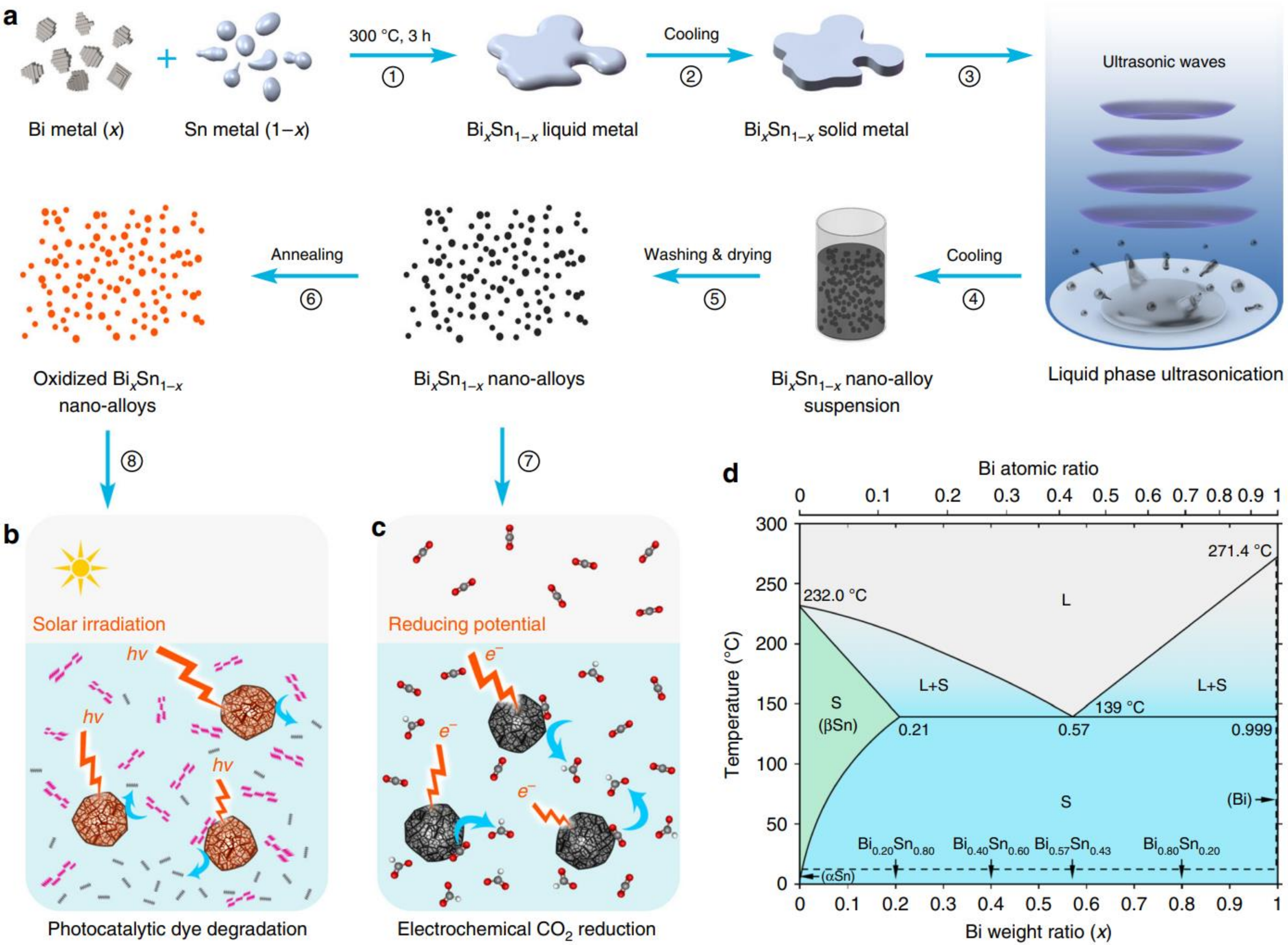
IIT Delhi
Department of Materials Science and Engineering

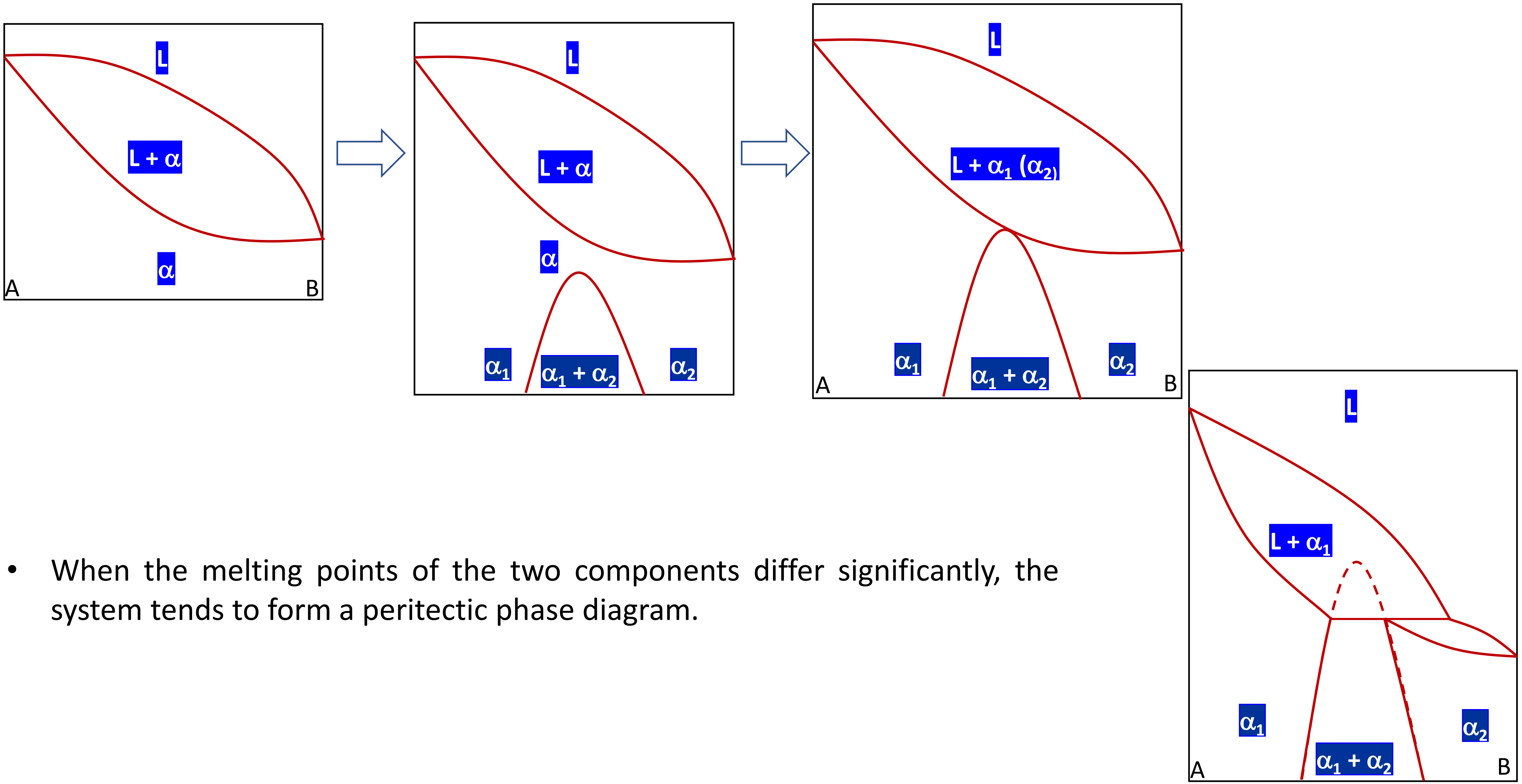
What have we learnt in Lecture-12?

- ❑ Eutectic phase diagram



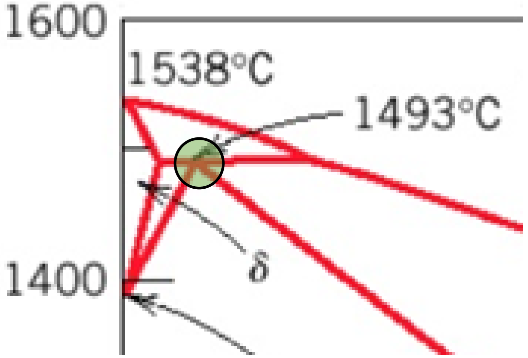
a
300 °C, 3 h
①
Cooling
②
③
Bi metal (x)
Sn metal (1−x)
Bi$_x$Sn$_{1-x}$ liquid metal
Bi$_x$Sn$_{1-x}$ solid metal
Ultrasonic waves
Liquid phase ultrasonication
Cooling
④
Washing & drying
⑤
Annealing
⑥
Oxidized Bi$_x$Sn$_{1-x}$ nano-alloys
Bi$_x$Sn$_{1-x}$ nano-alloys
Bi$_x$Sn$_{1-x}$ nano-alloy suspension
⑧
⑦
b
Solar irradiation
hv
Photocatalytic dye degradation
c
Reducing potential
e⁻
Electrochemical CO_2 reduction
d
Bi atomic ratio
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1
Temperature (°C)
300 250 200 150 100 50 0
271.4 °C
232.0 °C
L
L+S
L+S
S
(βSn)
139 °C
0.21
0.57
0.999
S
(Bi)
(αSn)
Bi$_{0.20}$Sn$_{0.80}$
Bi$_{0.40}$Sn$_{0.60}$
Bi$_{0.57}$Sn$_{0.43}$
Bi$_{0.80}$Sn$_{0.20}$
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1
Bi weight ratio (x)

Isomorphous ⟶ Peritectic phase diagram



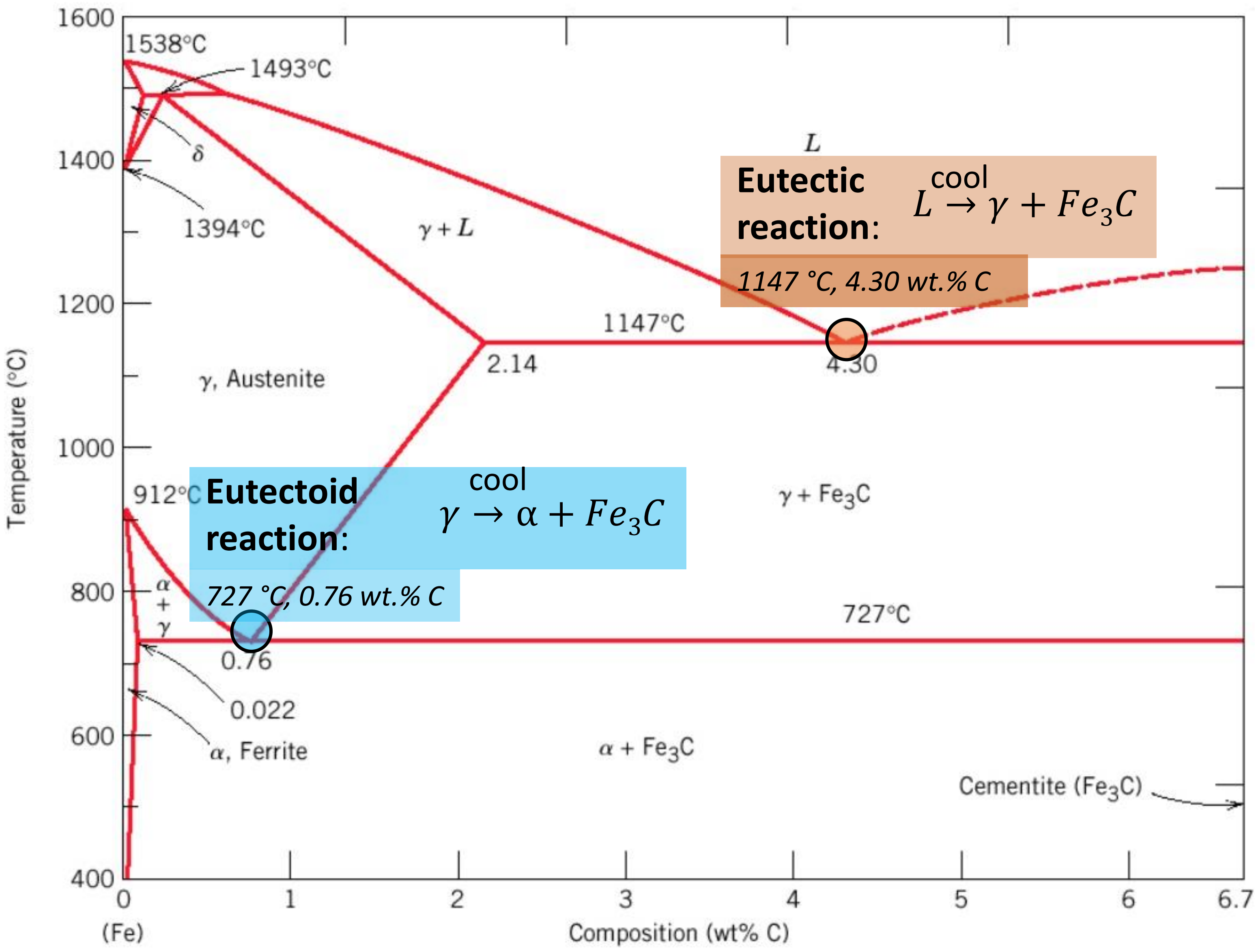
- When the melting points of the two components differ significantly, the system tends to form a peritectic phase diagram.

Iron-carbon phase diagram



Peritectic reaction: $L + \delta \xrightarrow{\text{cool}} \gamma$

1493 °C, 0.16 wt.% C



Eutectic reaction: $L \xrightarrow{\text{cool}} \gamma + Fe_3C$

1147 °C, 4.30 wt.% C

Eutectoid reaction: $\gamma \xrightarrow{\text{cool}} \alpha + Fe_3C$

727 °C, 0.76 wt.% C

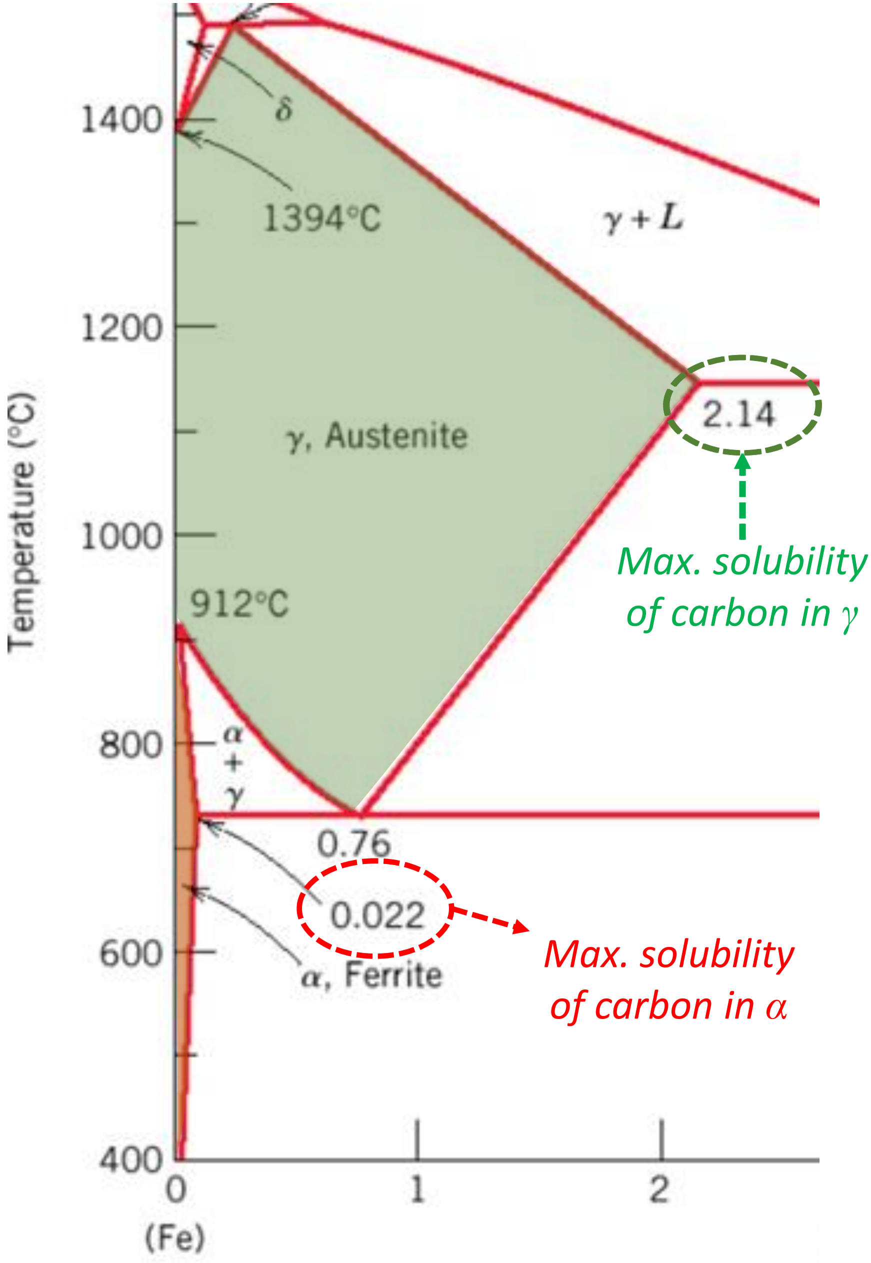
The 'Eutectoid reaction' holds technological significance.

- ❑ Why the solubility of 'Carbon' is more in the austenite phase (FCC) than in ferrite (BCC)??
- ❑ How does a carbon atom dissolve in an iron matrix?

- Carbon occupies the ***interstitial sites*** in an iron crystal structure.

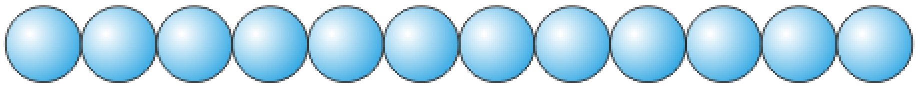
  Atomic radius of a carbon atom = 70 pm

- Volume fraction of BCC = 68%
- Volume fraction of FCC = 74%
- Empty space is higher in BCC.

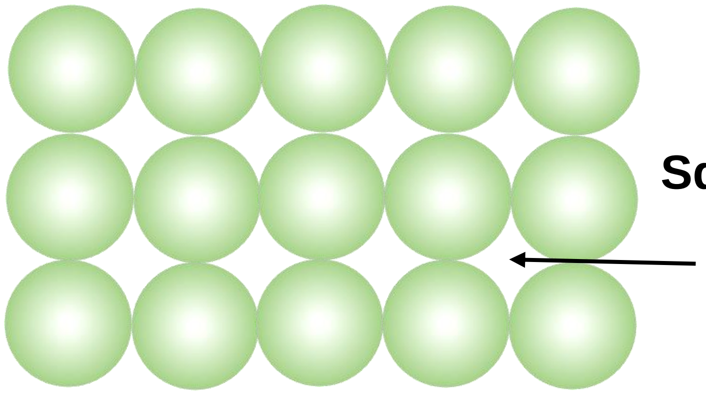


Packing sequence in cubic lattices

- **Close-packing in 1-D**

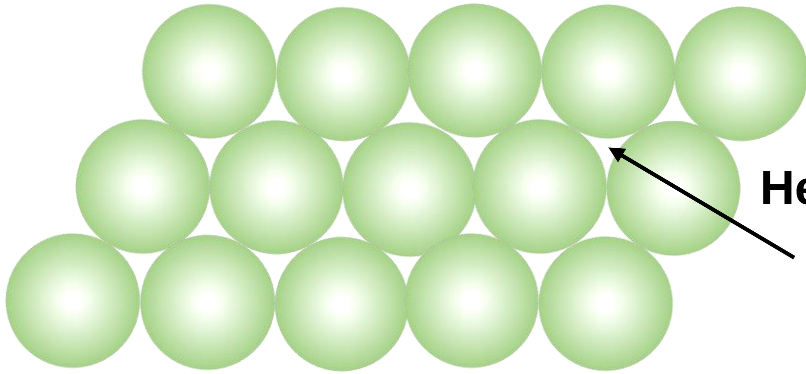


- **Close-packing in 2-D**



Square (primitive) packing

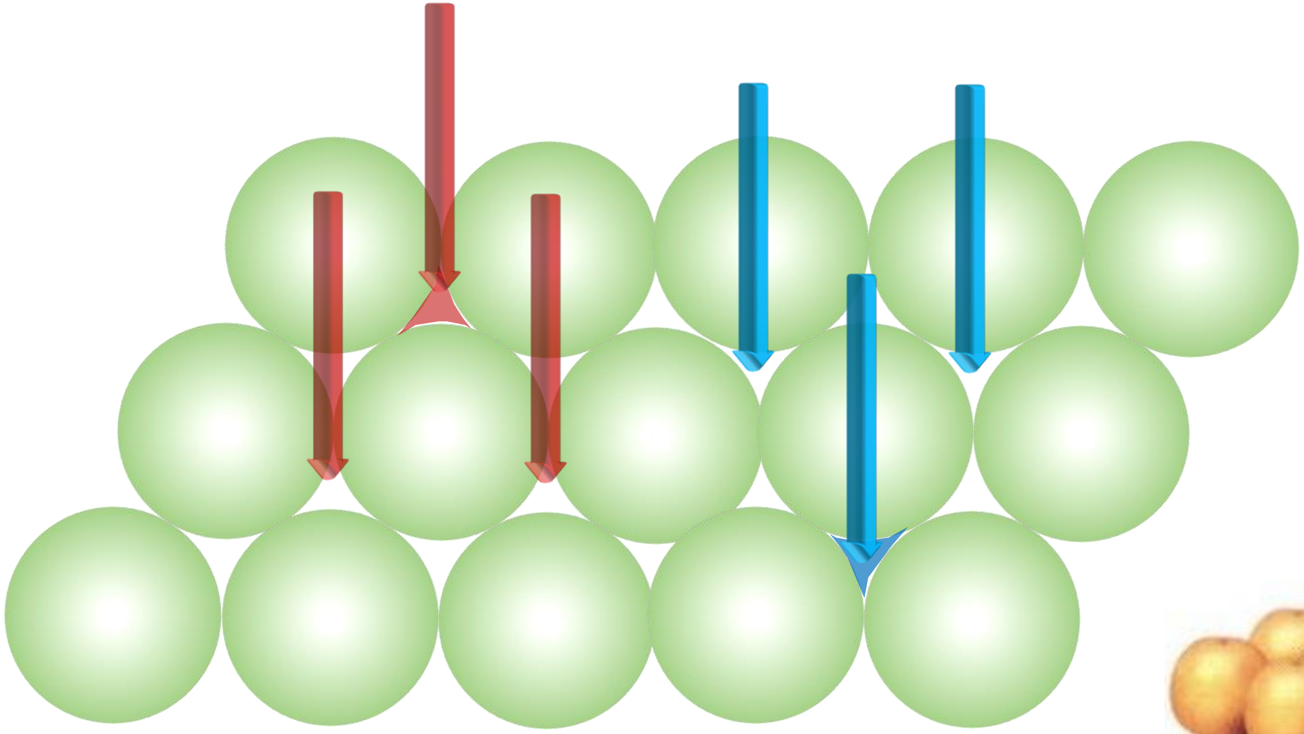
Large voids, low space-filling

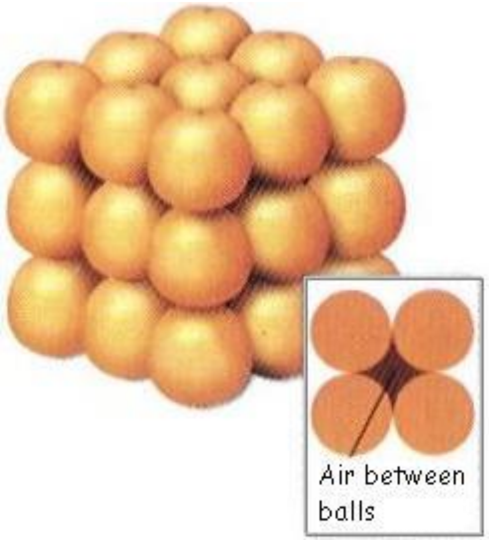


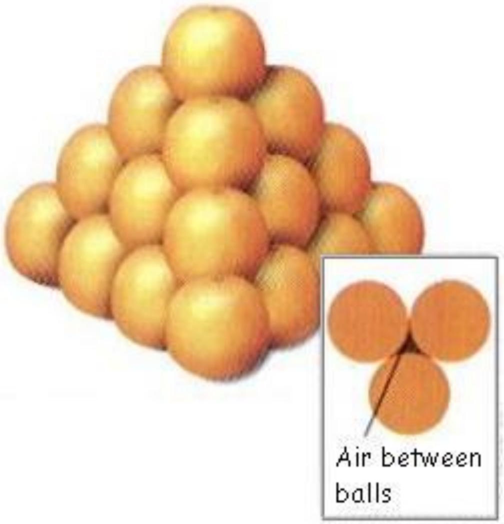
Hexagonal close packing

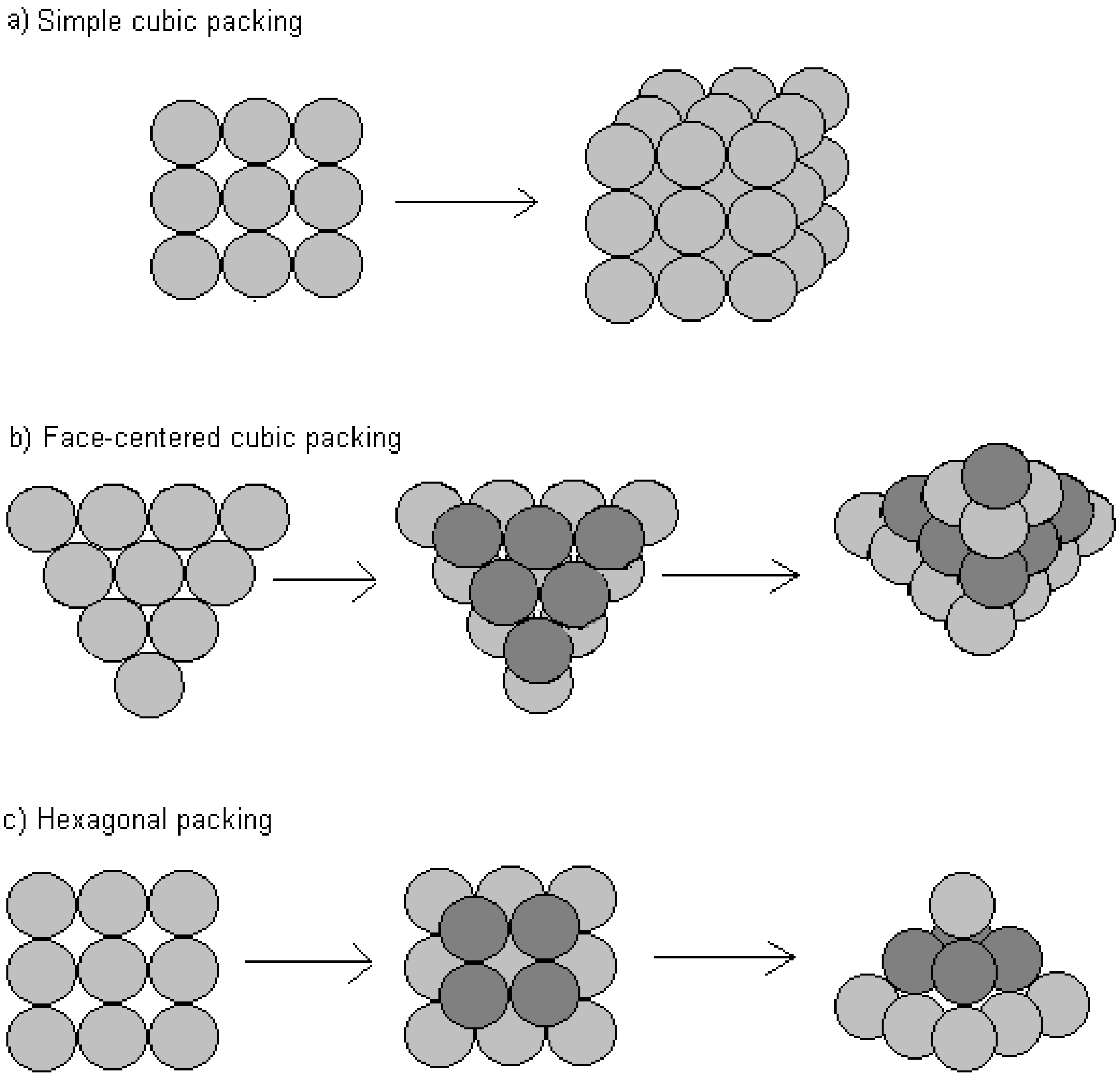
Small voids, high space-filling

- **Close-packing in 3-D ??**

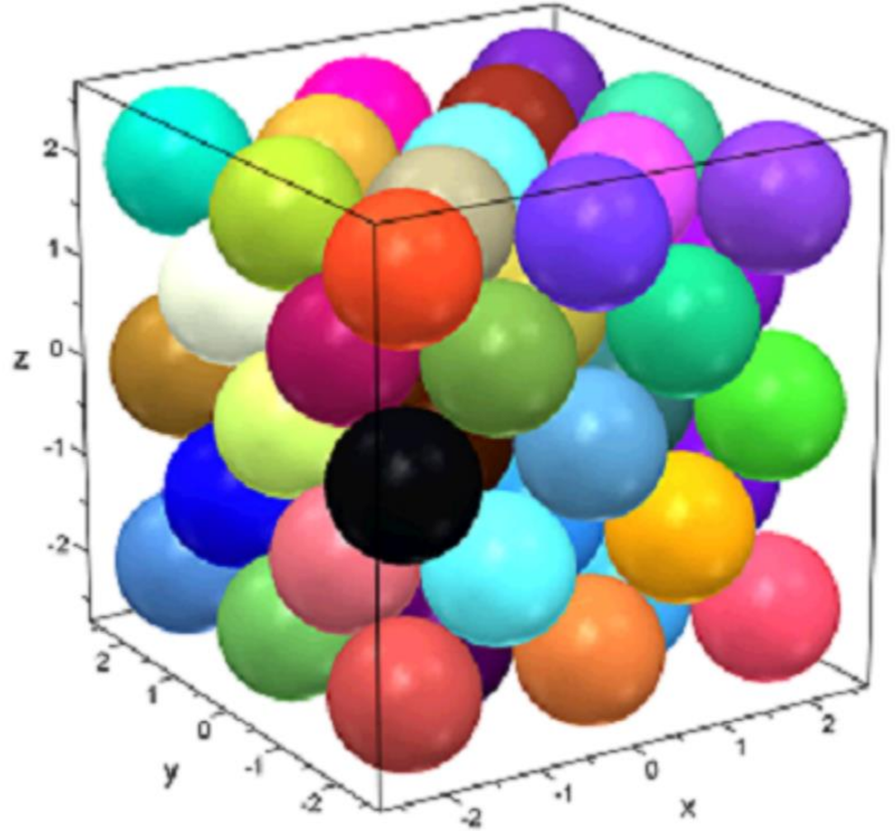






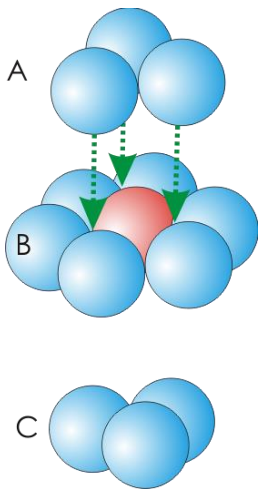


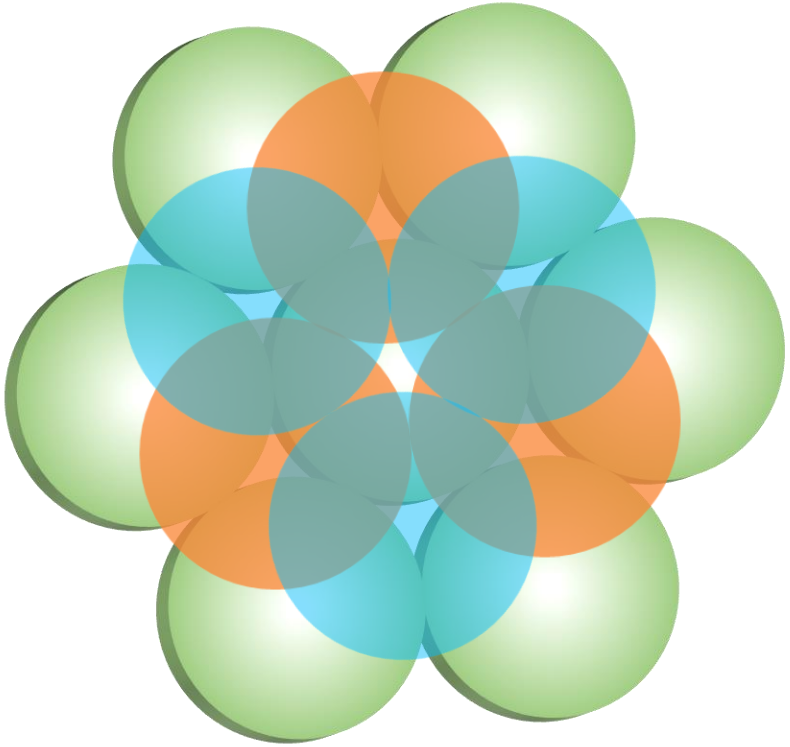
a) Simple cubic packing
b) Face-centered cubic packing
c) Hexagonal packing

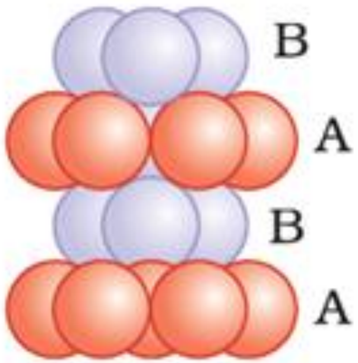


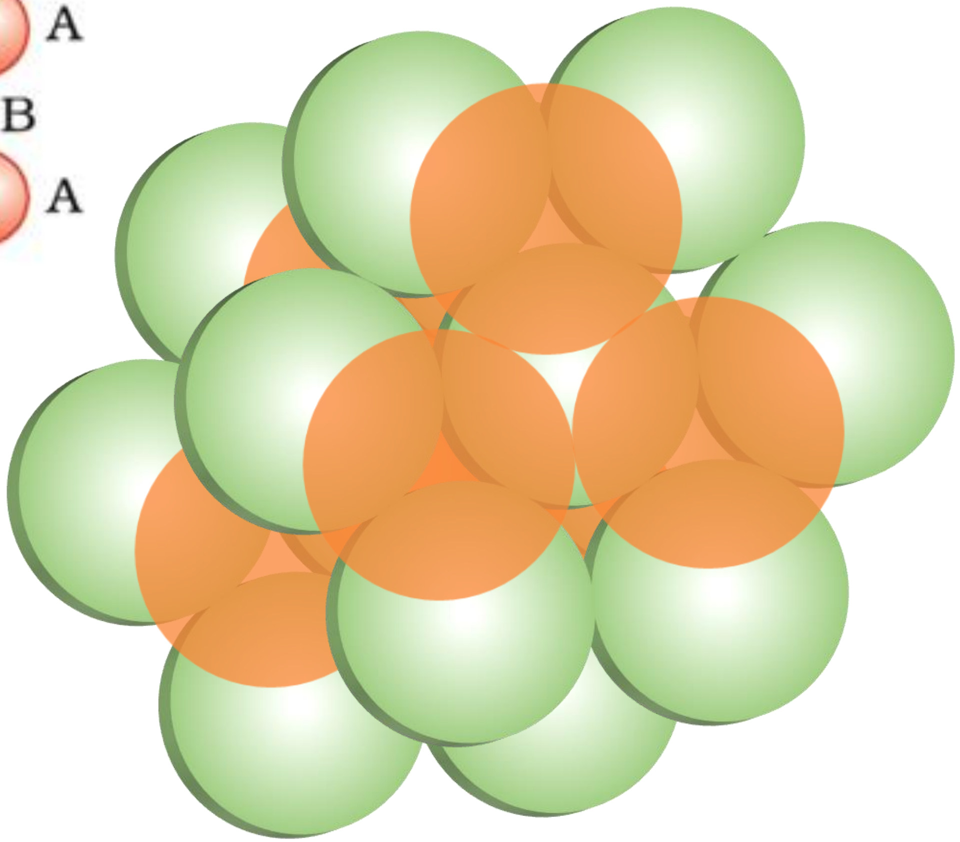
z
y
x

Close-packing in 3-D



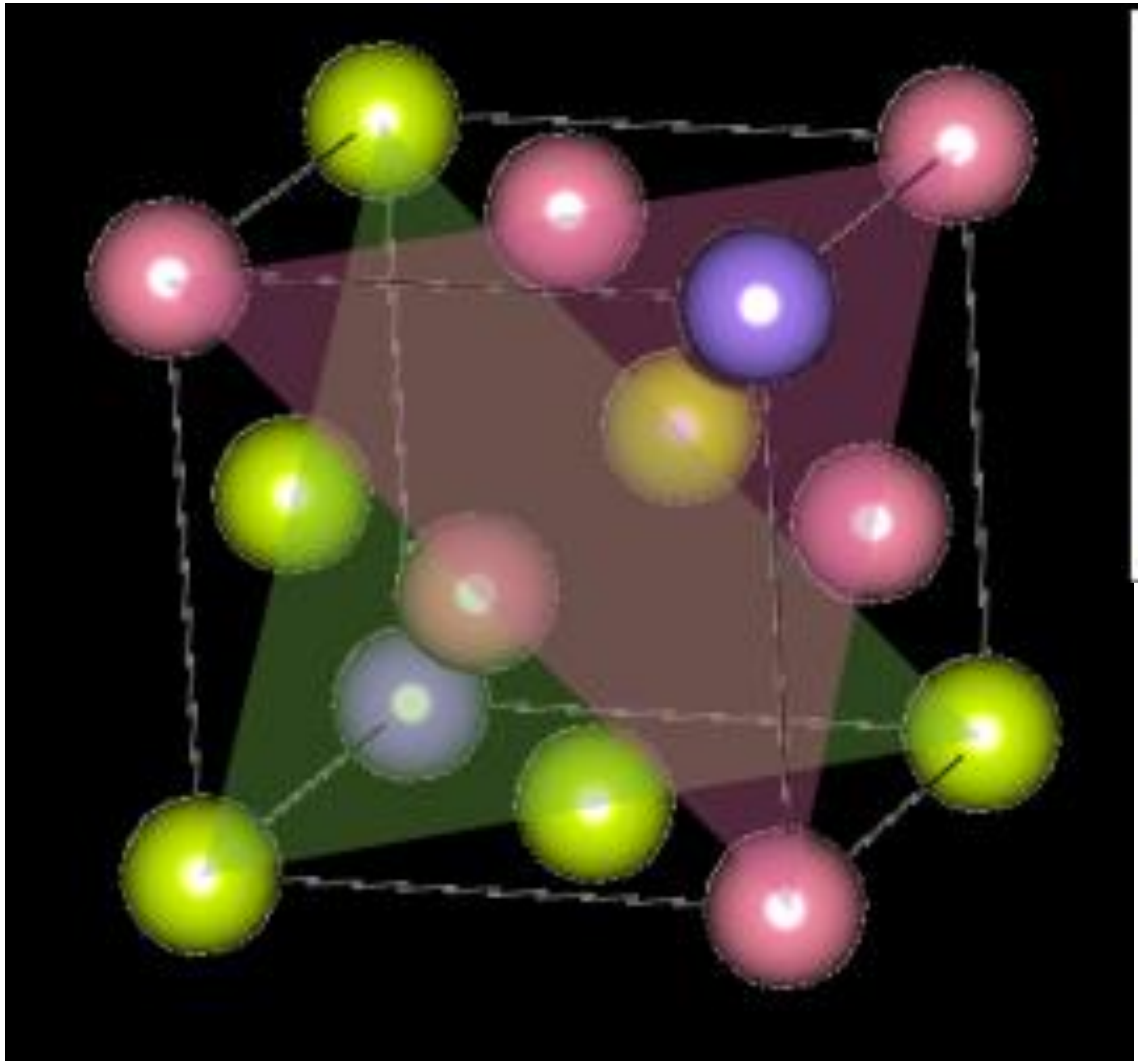


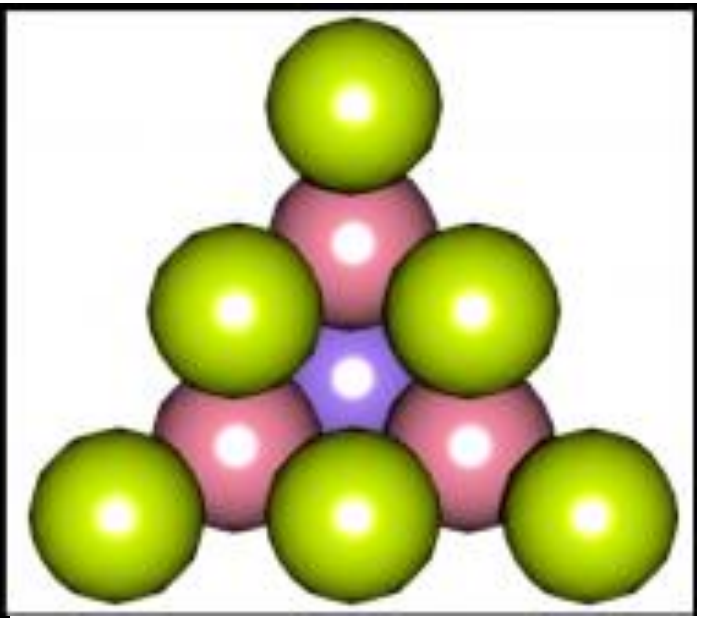




Stacking sequence	ABCABC…..	ABAB…..
Close packing type	Cubic close packing (CCP)	Hexagonal close packing (HCP)

Face-centred cubic

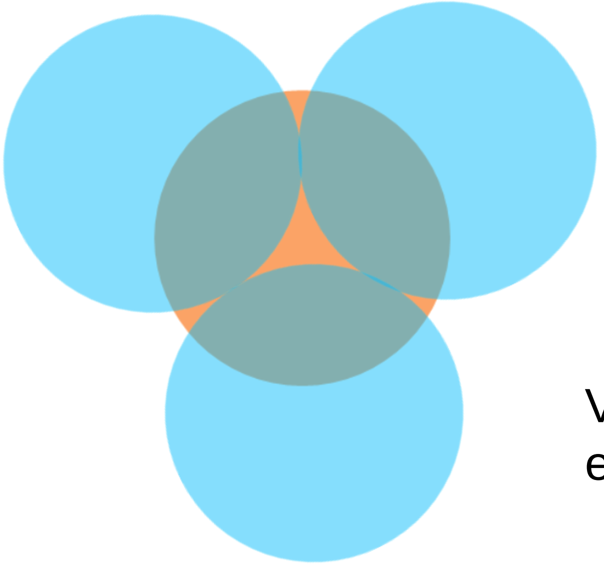


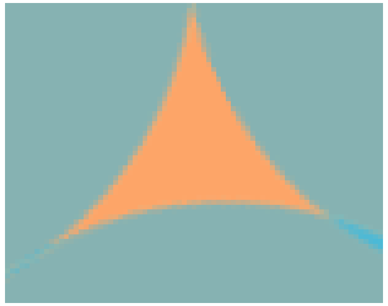


- Close-packed plane in FCC: {111}
- Close-packed direction in FCC: <110>

Empty spaces enclosed by atoms in a crystal: Voids

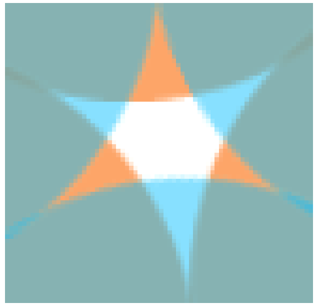
Voids in close-packed structures





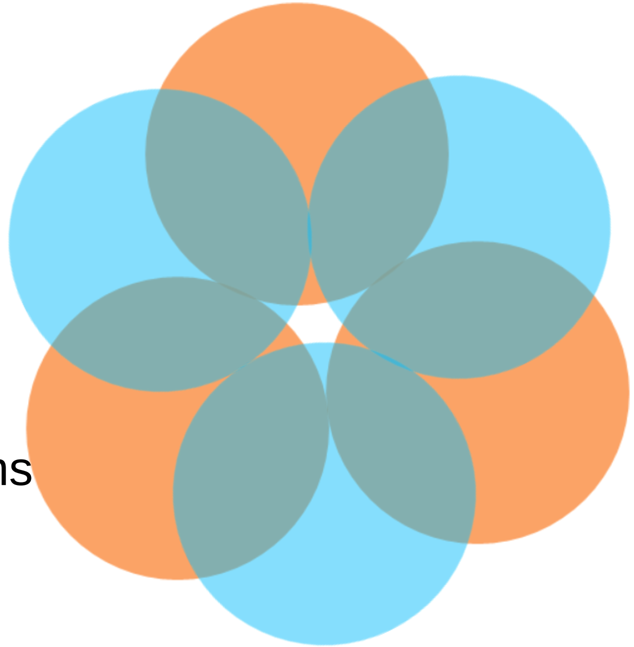
Tetrahedral void
(TV)

Void forms with 4 atoms enclosing the space



Octahedral void
(OV)

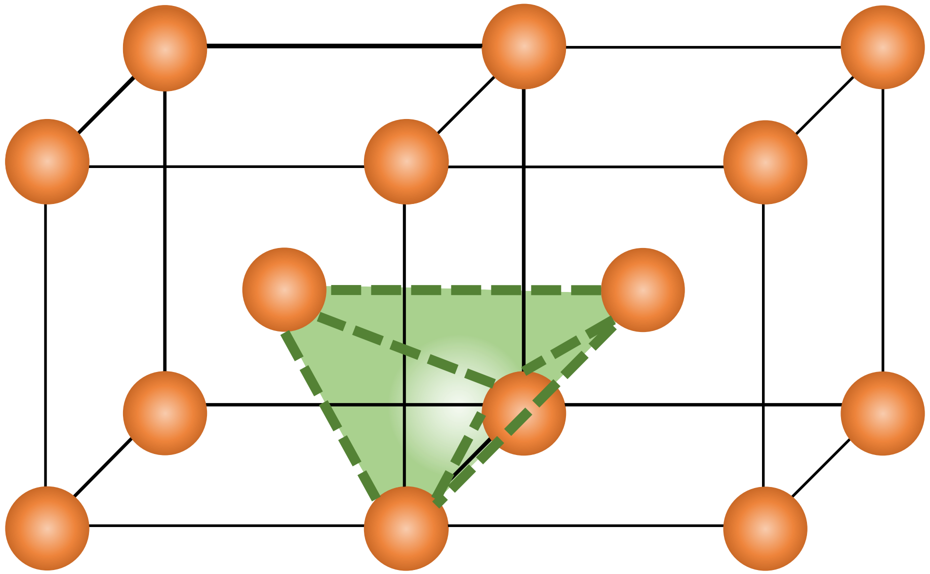
Void forms with 6 atoms enclosing the space



Co-ordination number **4** **6**

How many tetrahedral and octahedral voids are present in ferrite (BCC) and austenite (FCC)?

Tetrahedral voids in BCC



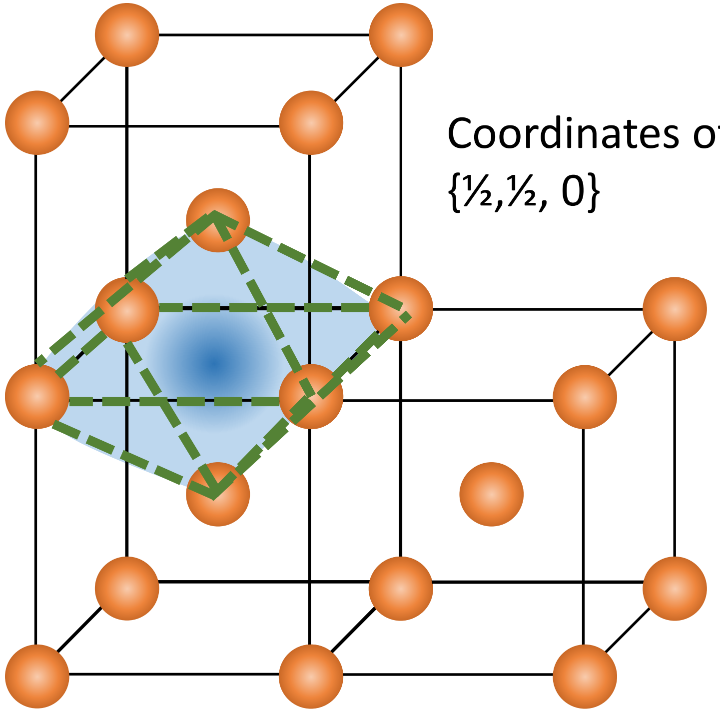
Coordinates of the void:
{½, 0, ¼} *(four on each face)*

- No. of faces: 6

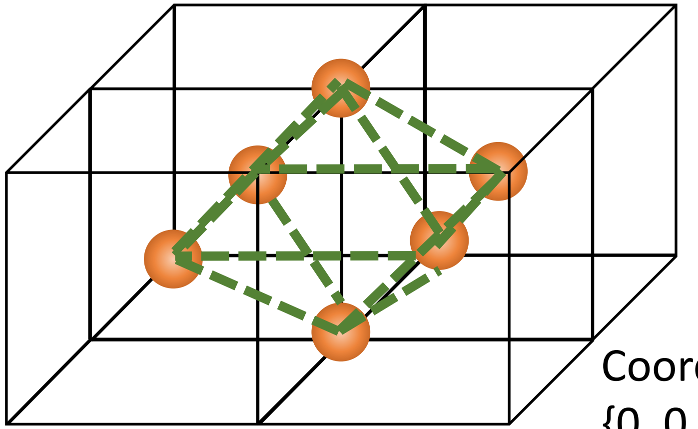
- Total no. of ‘T’ voids: 24
- No. of ‘T’ voids per unit cell : (24/2) = 12

- No. of ‘T’ voids per unit atom: (12/2) = 6

Octahedral voids in BCC

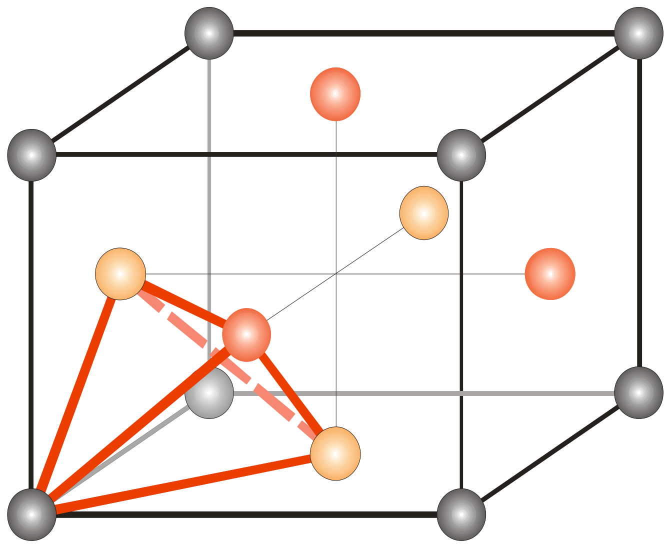


Coordinates of the void:
{½,½, 0}

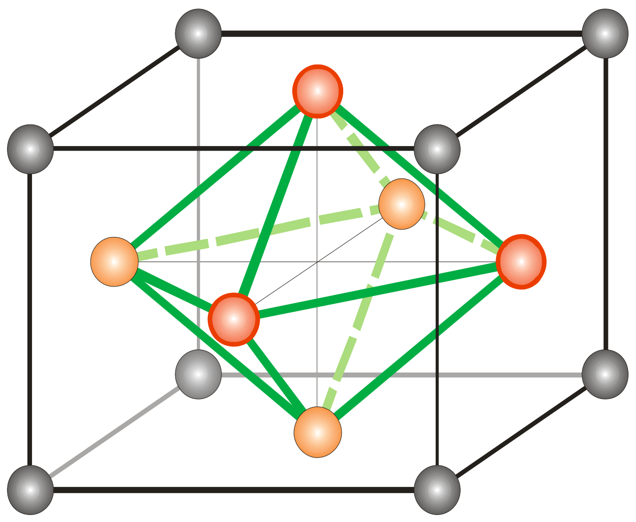


Coordinates of the void:
{0, 0, ½}

Tetrahedral voids in FCC



Octahedral voids in FCC



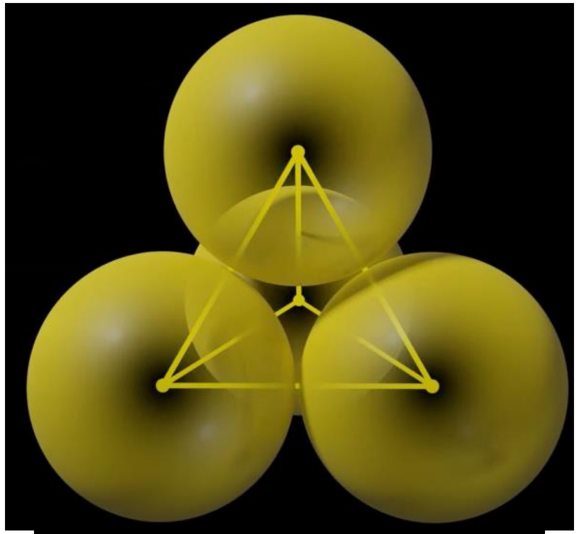
Number of voids in BCC and FCC

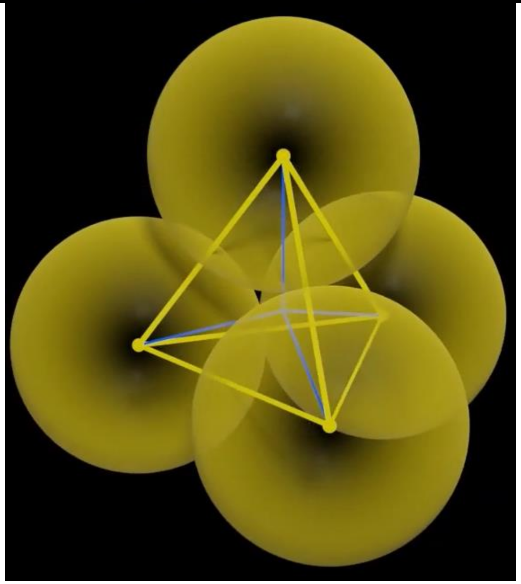
BCC voids	Position	Voids / cell	Voids / atom
Distorted Tetrahedral	• Four on each face: [(4/2) × 6 = 12] → (0, ½, ¼)	12	6
Distorted Octahedral	• Face center: (6/2 = 3) → (½, ½, 0) • Edge center: (12/4 = 3) → (½, 0, 0)	6	3

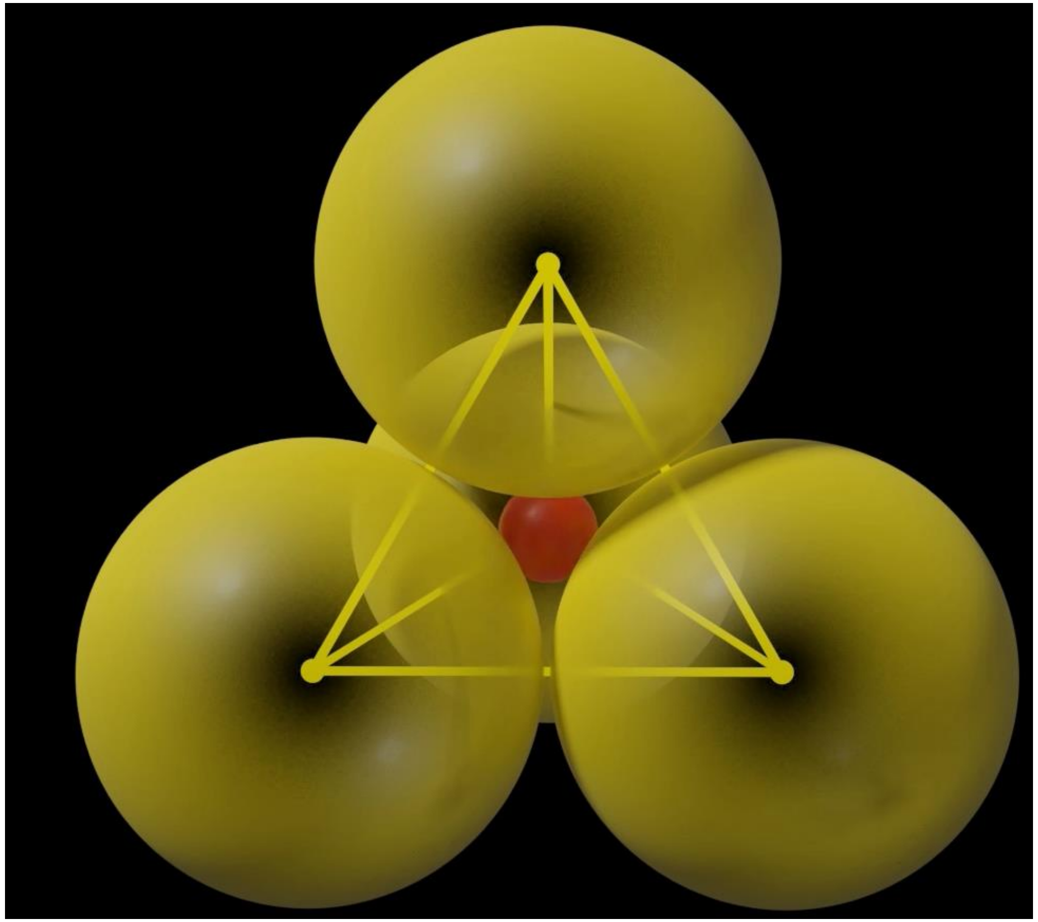
FCC voids	Position	Voids / cell	Voids / atom
Tetrahedral	¼ way from each vertex of the cube along body diagonal <111> → ((¼, ¼, ¼))	8	2
Octahedral	• Body centre: 1 → (½, ½, ½) • Edge centre: (12/4 = 3) → (½, 0, 0)	4	1

- ❑ Number of 'T' voids is greater than those of 'O' voids.
- ❑ But, still Carbon prefers to occupy the 'O' voids.

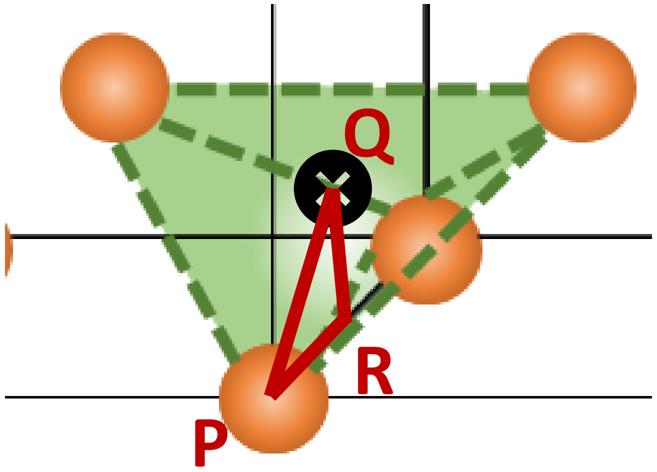
What is the size of the largest atom which can fit into a tetrahedral void of BCC?







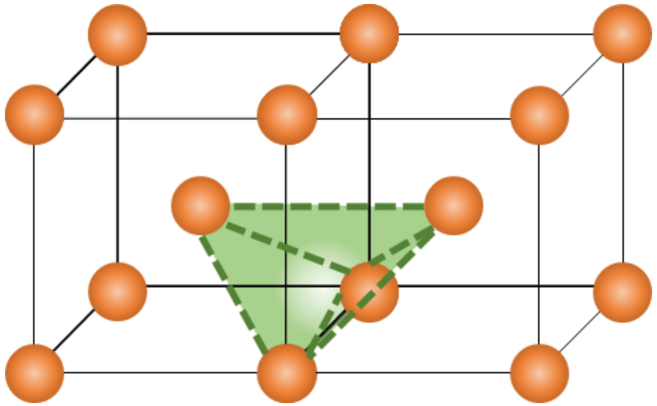
What is the size of the largest atom which can fit into a tetrahedral void of BCC?



Consider ΔPQR,

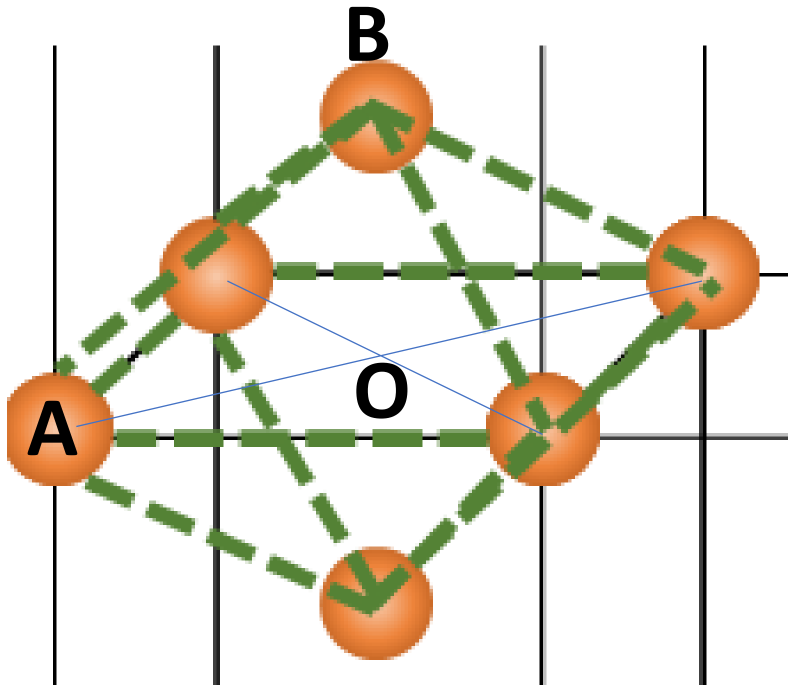
$$PQ = \sqrt{\frac{a^2}{(4)^2} + \left(\frac{a^2}{4}\right)} = (r + x) = \frac{\sqrt{5}}{4}.a$$

In a BCC crystal system, $a = \frac{4.r}{\sqrt{3}}$

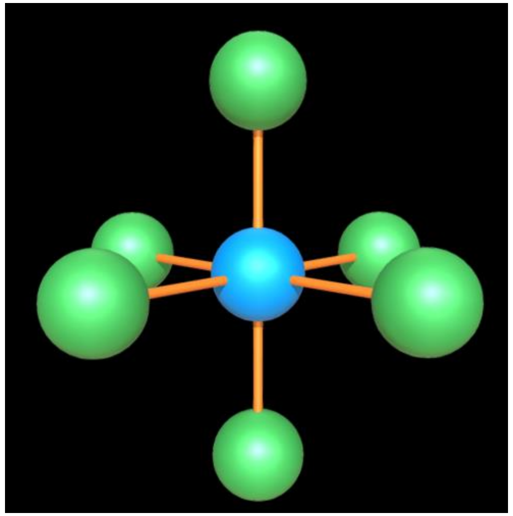


$$x = 0.29.r$$

What is the size of the largest atom which can fit into a octahedral void of BCC?



- Distance (OA) = $\frac{a}{\sqrt{2}}$ = 0.707 a
- Distance (OB) = $(\frac{a}{2})$ = 0.5 a
- Since the length of OB is smaller than OA, the atom situated at the Octahedral void is expected to touch the body-centred atom (point 'B').

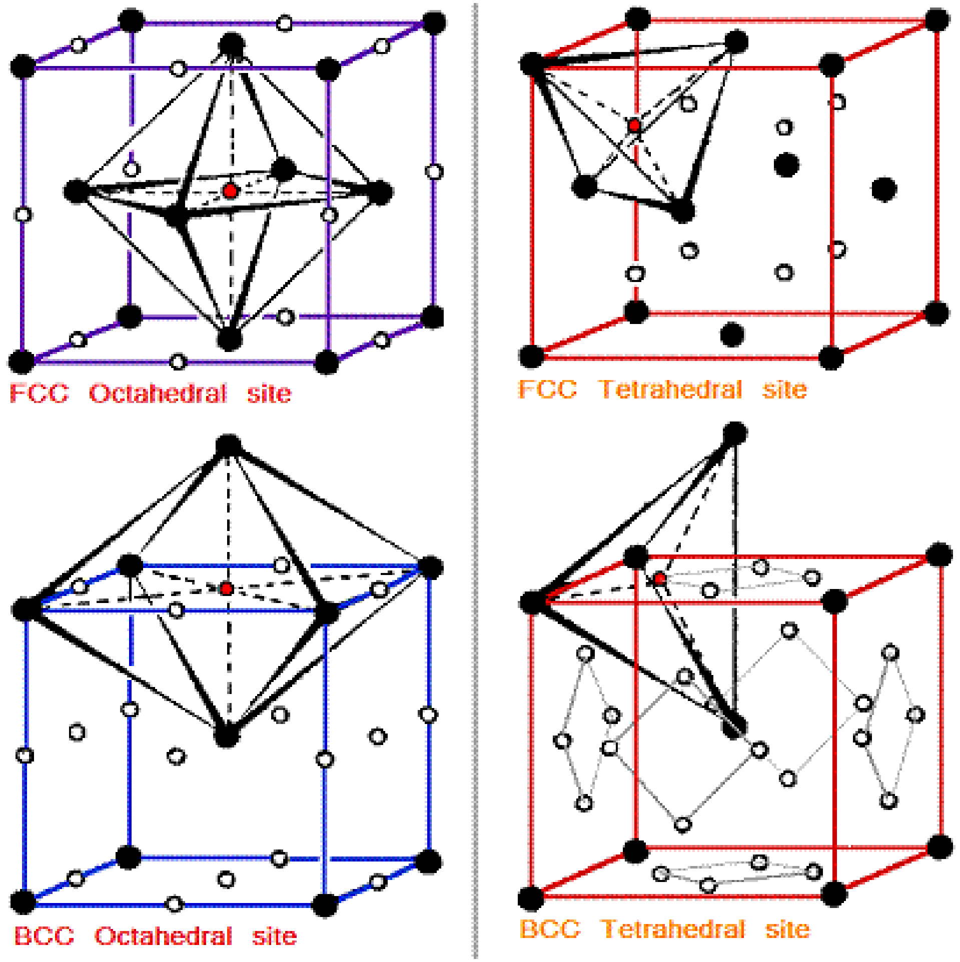


$$OB = r + x = \frac{a}{2}$$

$$r + x = \frac{4r}{2\sqrt{3}} \qquad BCC : \sqrt{3}a = 4r$$

$$\frac{x}{r} = \left(\frac{2\sqrt{3}}{3} - 1\right) = 0.1547$$

BCC voids	Position	Voids / cell	Voids / atom
Distorted Tetrahedral	• Four on each face: [(4/2) × 6 = 12] → (0, ½, ¼)	12	6
Distorted Octahedral	• Face center: (6/2 = 3) → (½, ½, 0) • Edge center: (12/4 = 3) → (½, 0, 0)	6	3



	BCC	FCC
Octahedral	0.155 (*distorted*)	0.414
Tetrahedral	0.29 (*distorted*)	0.225

➢ ***Why interstitial atoms prefer to occupy the octahedral positions?***

Second QUIZ of MLL100

Date	: *February 12, 2022*
Day	: *Saturday*
Time	: *10:30 a.m. – 10:45 a.m.*
Marks	: *10*
Mode	: *Online (Moodle)*
Syllabus	: *Phase equilibria, Phase diagrams and Phase transformations*

MLL 100

Introduction to Materials Science and Engineering

Lecture-14 (February 08, 2022)

Dr. Sangeeta Santra (*ssantra@mse.iitd.ac.in*)

IIT Delhi
Department of Materials Science and Engineering

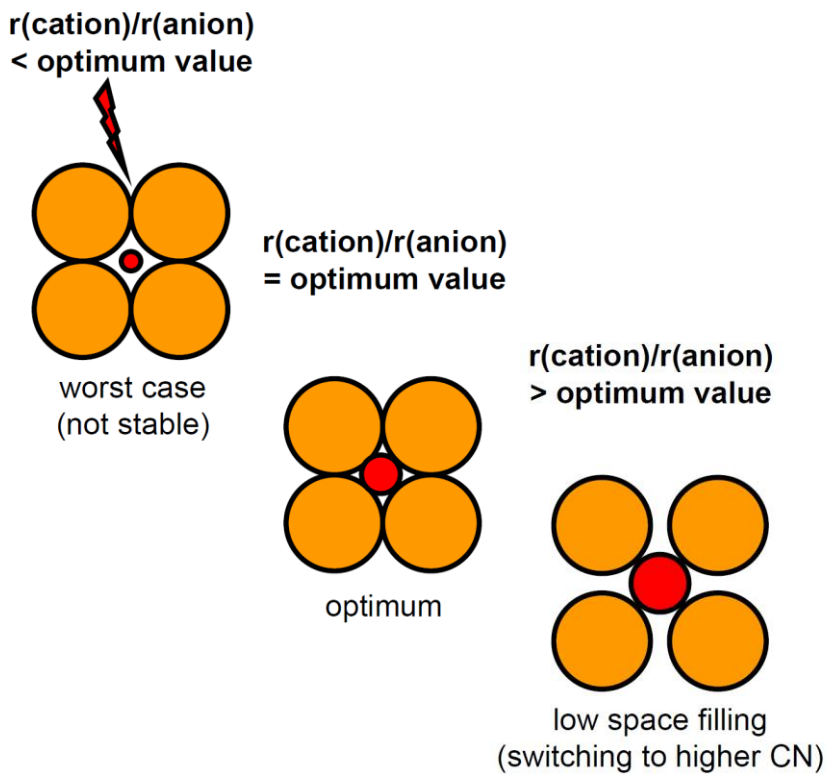
What have we learnt in Lecture-13?

- ❑ Peritectic phase diagram

  Monotectic reaction: L_1 ---------> $L_2 + S$

- ❑ Voids: Tetrahedral and Octahedral

- ❑ Iron-carbon phase diagram



No Rattling — *Cation should not be smaller than the void formed by the anions*

↓

Cation size larger than the void — *Cation should be larger than the void so that the anions do not touch each other*

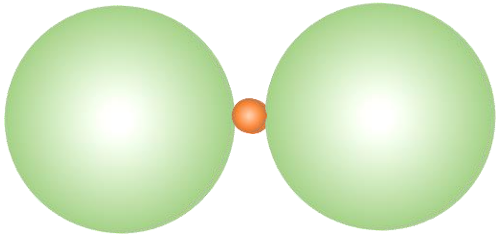
↓

Choose the largest coordination possible — *Largest coordination gives the best possible packing*

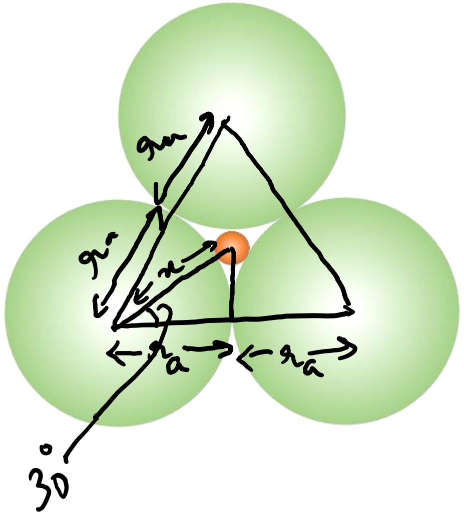
- Cations should surround themselves with as many anions as possible, and vice versa. This maximizes the attractions between neighbouring ions of opposite charge and hence maximizes the lattice energy of the crystal.

- *Radius ratio rule for ionic structures*

- A cation must be in contact with its neighbour anion -----> Lower limit on the size of a cation which may occupy a particular position.
- Neighbouring anions may or may not be in contact with each other.



$\frac{r_c}{r_a} = 0 - 0.155$



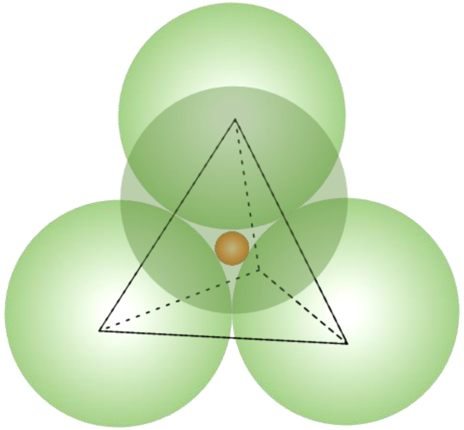
$\frac{r_c}{r_a} = 0.155 - 0.225$

Lower limit is governed by current coordination

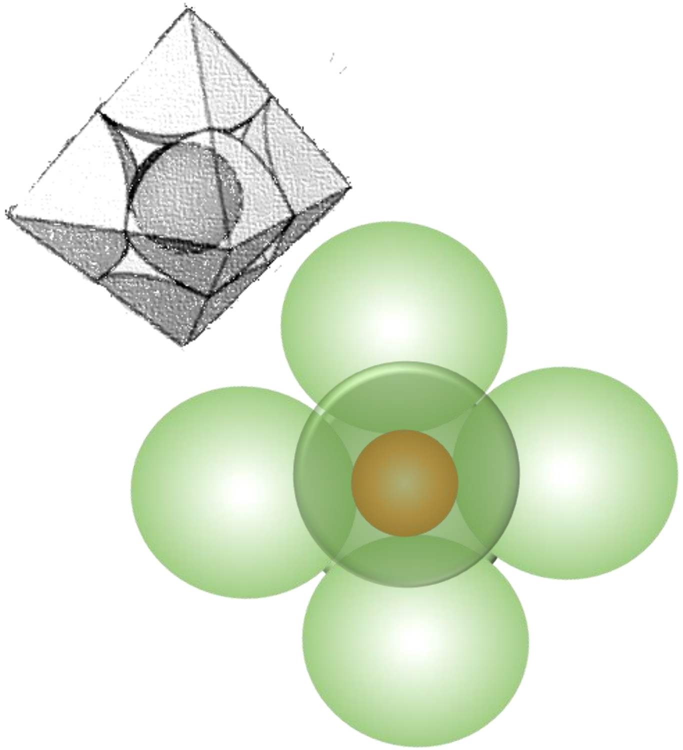
Upper limit is governed by next higher possible coordination

$$\cos 30^\circ = \frac{r_a}{(r_a + r_c)} = \frac{\sqrt{3}}{2}$$

$$\therefore \left(\frac{r_c}{r_a}\right) = 0.155$$



$\frac{r_c}{r_a} = 0.225 - 0.414$



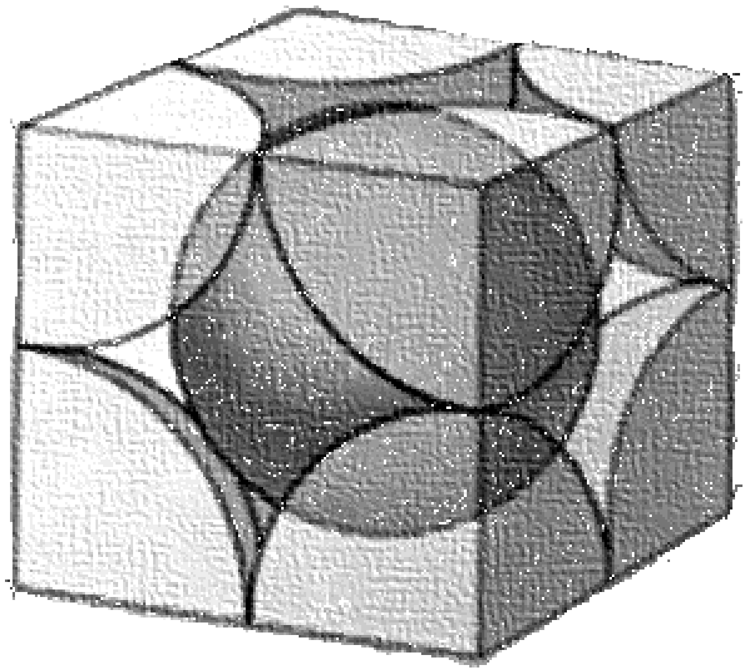
$\frac{r_c}{r_a} = 0.414 - 0.732$

$$(2r_a)^2 + (2r_a)^2 = \{2(r_a + r_c)\}^2$$

$$\therefore \quad 2\sqrt{2}\, r_a = 2(r_a + r_c)$$

$$\therefore (\sqrt{2} - 1)\, r_a = r_c$$

$$\therefore \left(\frac{r_c}{r_a}\right) = 0.414$$

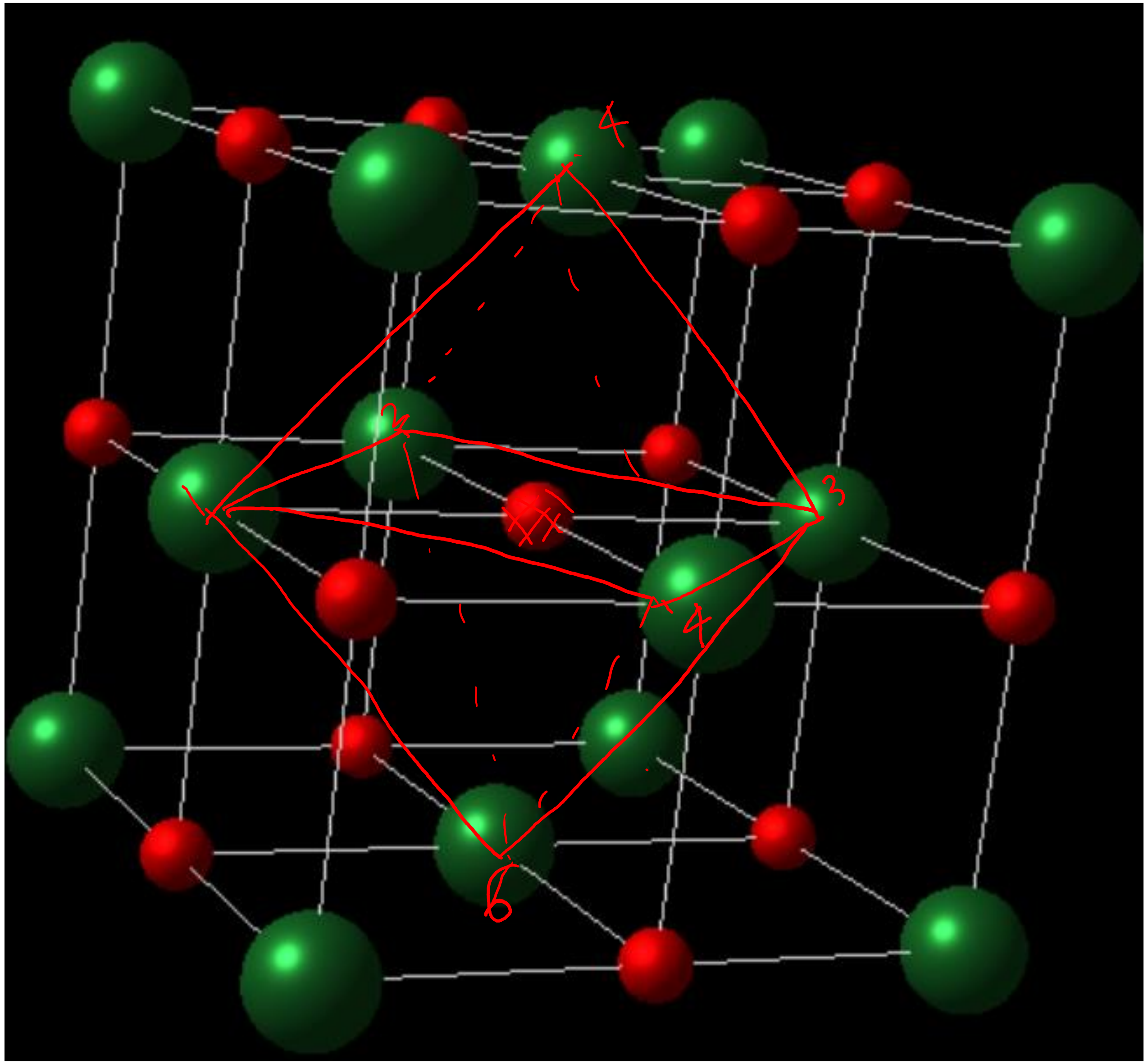


$$\frac{r_c}{r_a} = 0.732 - 1.0$$

$$(2r_c + 2r_a) = \text{Body diagonal}$$
$$= \sqrt{3}\,a = \sqrt{3}\,(2r_a)$$

$$\therefore \left(\frac{r_c}{r_a}\right) = 0.732$$

$\left(\frac{r_c}{r_a}\right)$	Co-ordination number (CN)	Geometry	Crystal structures
0 – 0.155	2	Linear	
0.155 – 0.225	3	Triangular	
0.225 – 0.414	4	Tetrahedron	
0.414 – 0.732	6	Octahedron	
0.732 – 1.0	8	Cube	

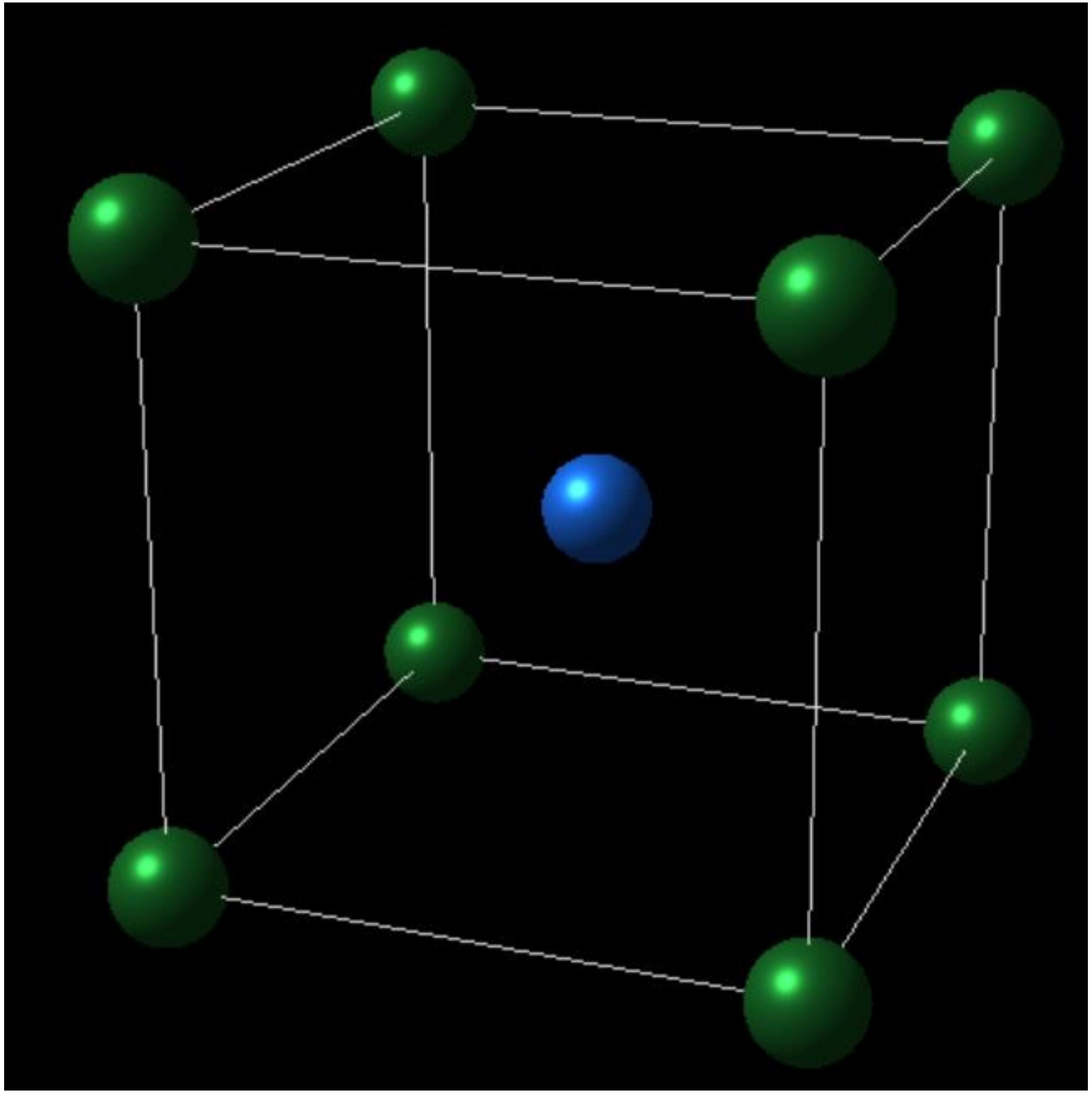


$r_{Na^+} = 0.102$ nm

$r_{Cl^-} = 0.181$ nm

$$\frac{r_{Na^+}}{r_{Cl^-}} = 0.56$$

$(\frac{r_c}{r_a})$	Co-ordination number (CN)	Geometry	Crystal structures
0 – 0.155	2	Linear	
0.155 – 0.225	3	Triangular	
0.225 – 0.414	4	Tetrahedron	
0.414 – 0.732	6	Octahedron	
0.732 – 1.0	8	Cube	

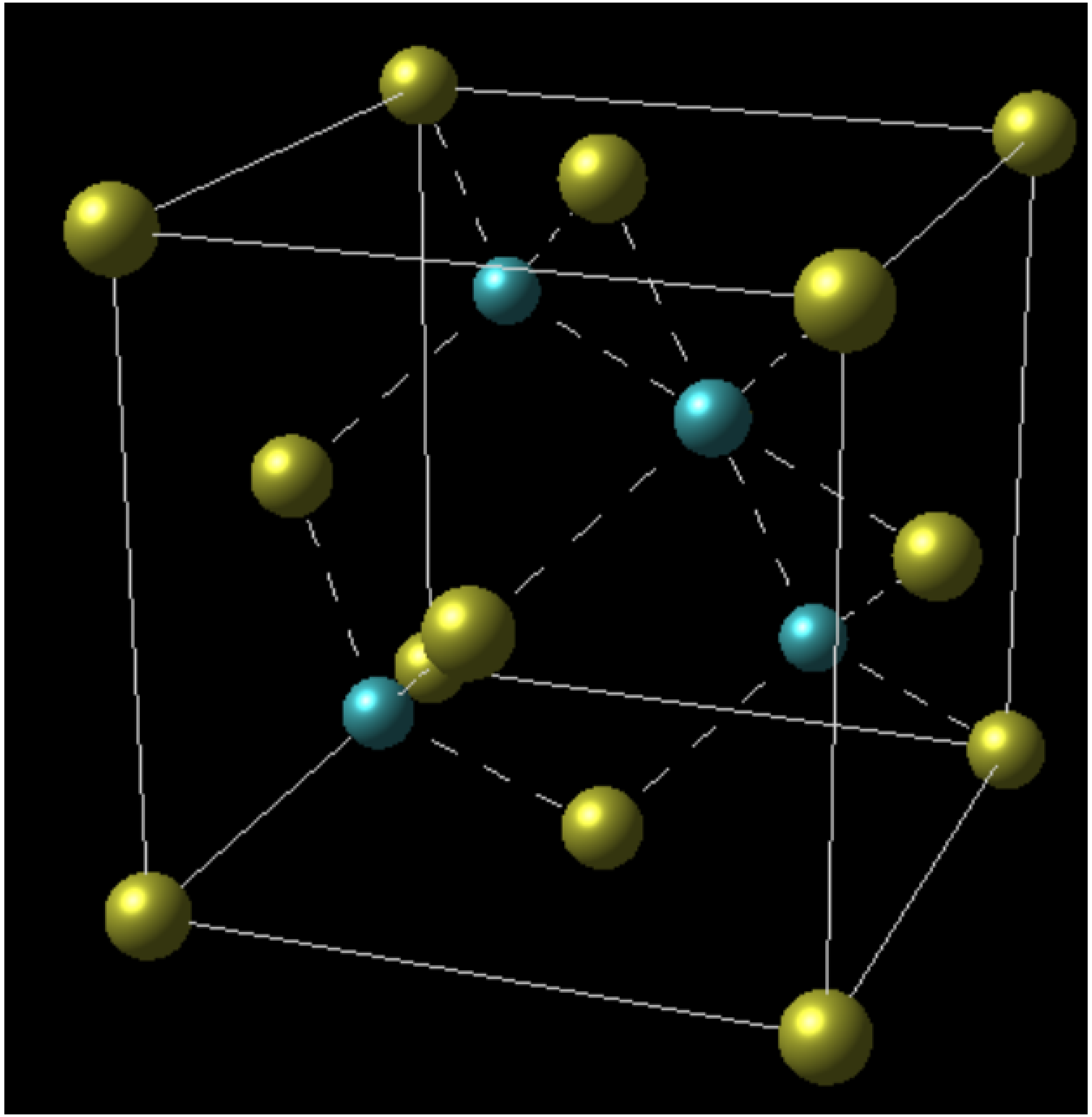


r_{Cs^+} = 0.167 nm

r_{Cl^-} = 0.181 nm

$$\frac{r_{Cs^+}}{r_{Cl^-}} = 0.92$$

$(\frac{r_c}{r_a})$	Co-ordination number (CN)	Geometry	Crystal structures
0 – 0.155	2	Linear	
0.155 – 0.225	3	Triangular	
0.225 – 0.414	4	Tetrahedron	
0.414 – 0.732	6	Octahedron	NaCl
0.732 – 1.0	8	Cube	



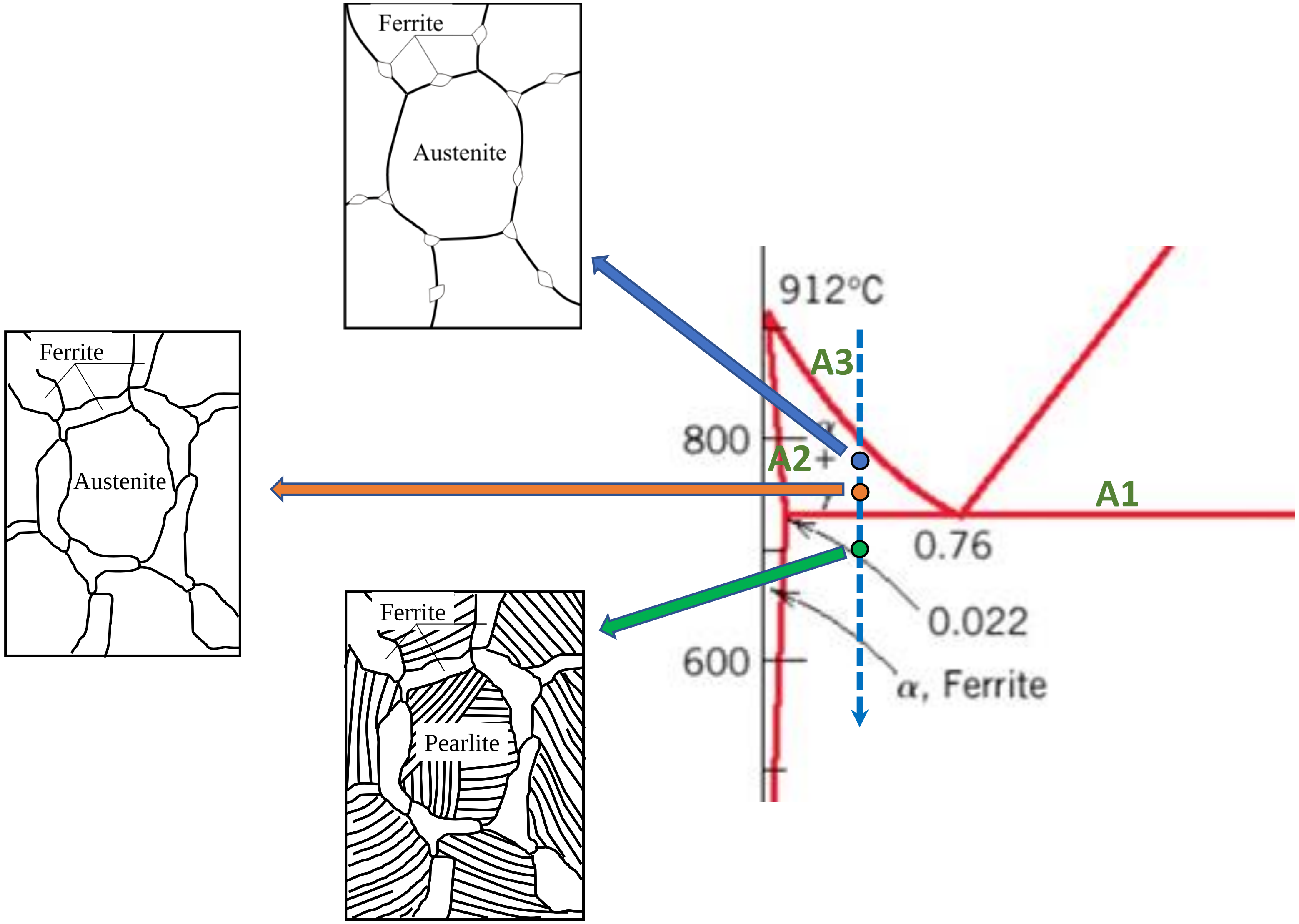
$$r_{Zn^{2+}} = 0.074 \text{ nm}$$
$$r_{S^{2-}} = 0.184 \text{ nm}$$

$$\frac{r_{Zn^{2+}}}{r_{S^{2-}}} = 0.40$$

$(\frac{r_c}{r_a})$	Co-ordination number (CN)	Geometry	Crystal structures
0 – 0.155	2	Linear	
0.155 – 0.225	3	Triangular	
0.225 – 0.414	4	Tetrahedron	
0.414 – 0.732	6	Octahedron	NaCl
0.732 – 1.0	8	Cube	CsCl

How does different phases evolve microstructurally in an Fe-C system?

Microstructural evolution of a hypoeutectic alloy

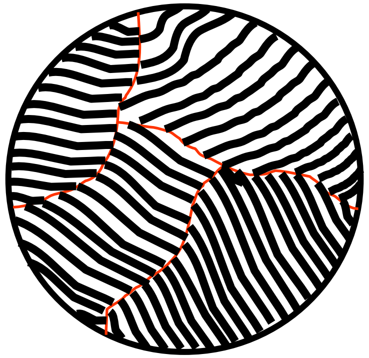


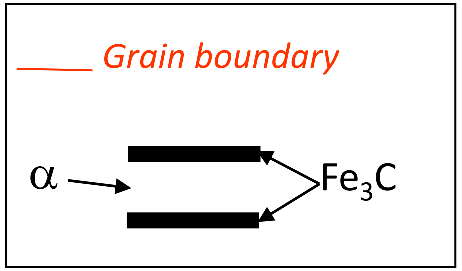
- On crossing the 'A3' line, the ferrite phase starts appearing on the austenite grain boundaries.
- ***Why at the grain boundaries?***

- The ferrite phase grows along the grain boundaries, and slowly protrude inside the grains of austenite.

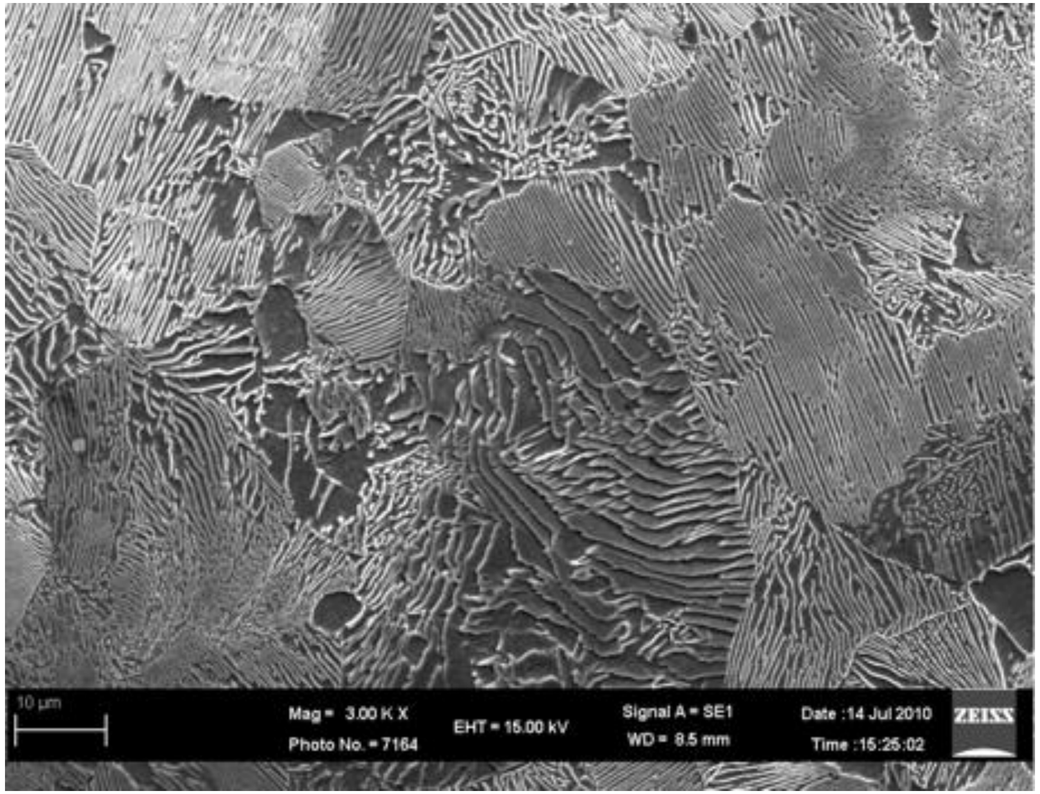
- On crossing the 'A1' line, the remaining austenite transforms to 'ferrite and cementite'.
- ***Why 'pearlite' is mentioned in the schematic microstructure?***

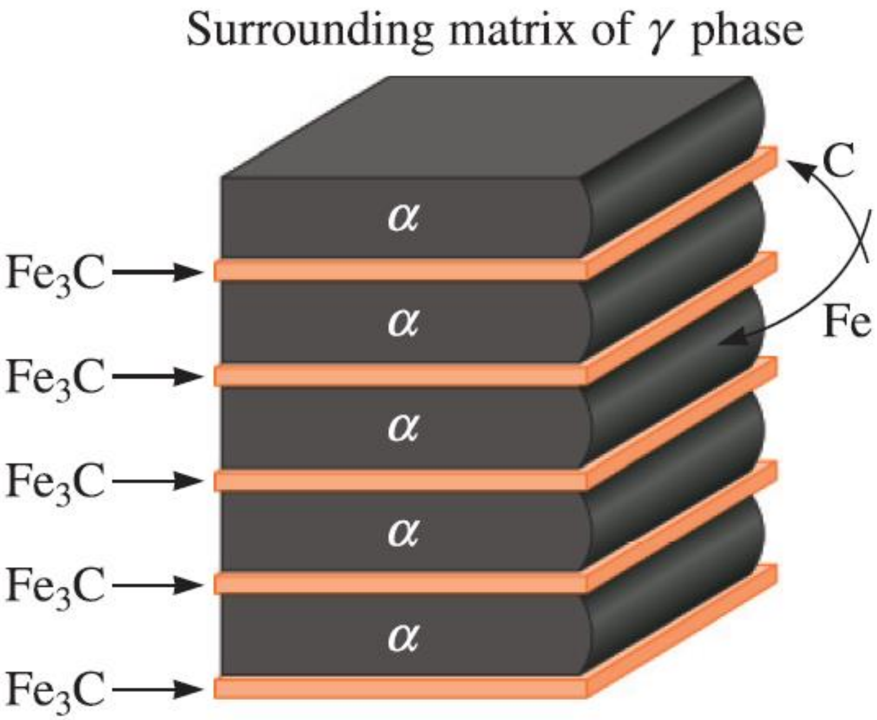
Pearlite

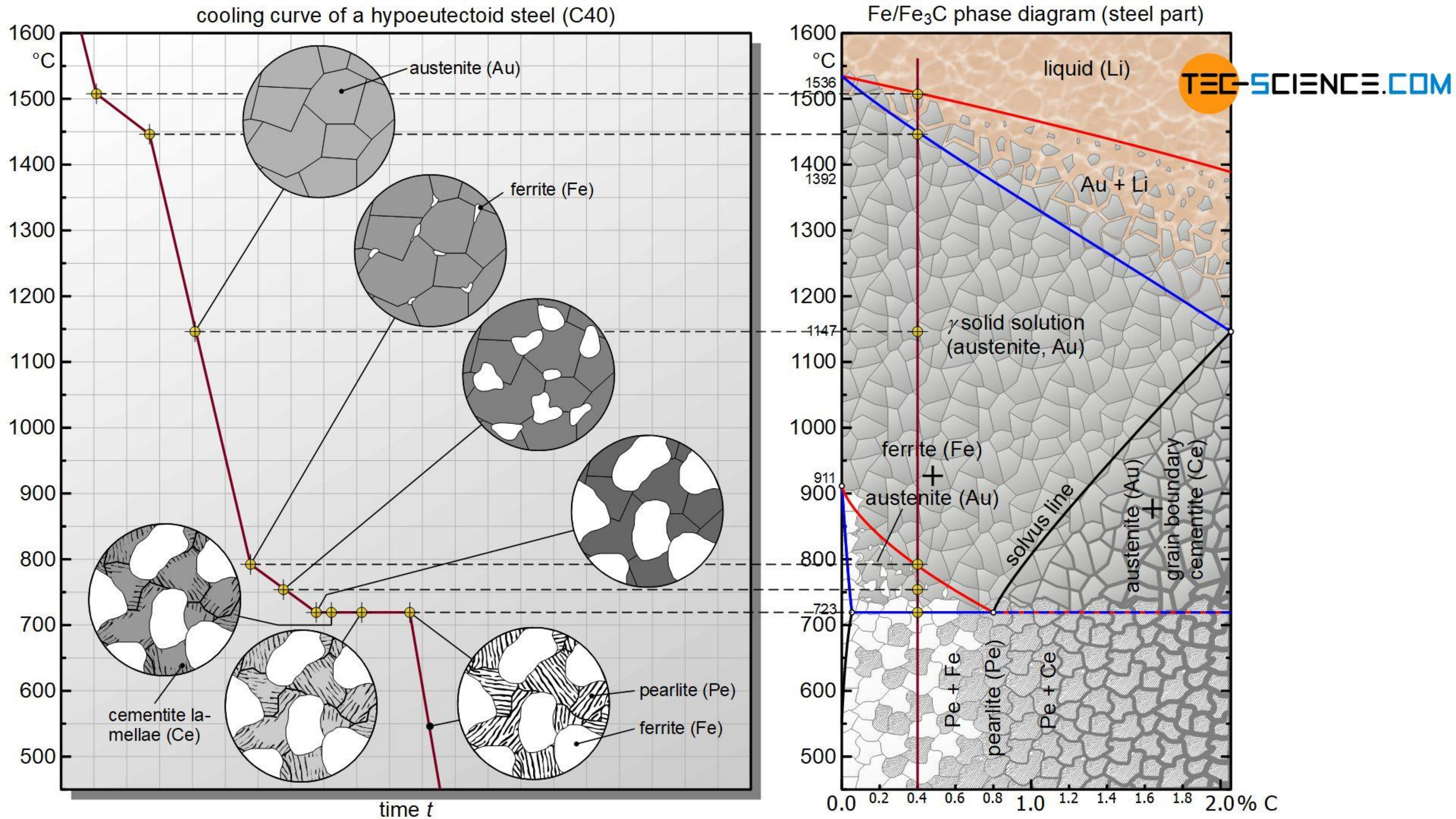


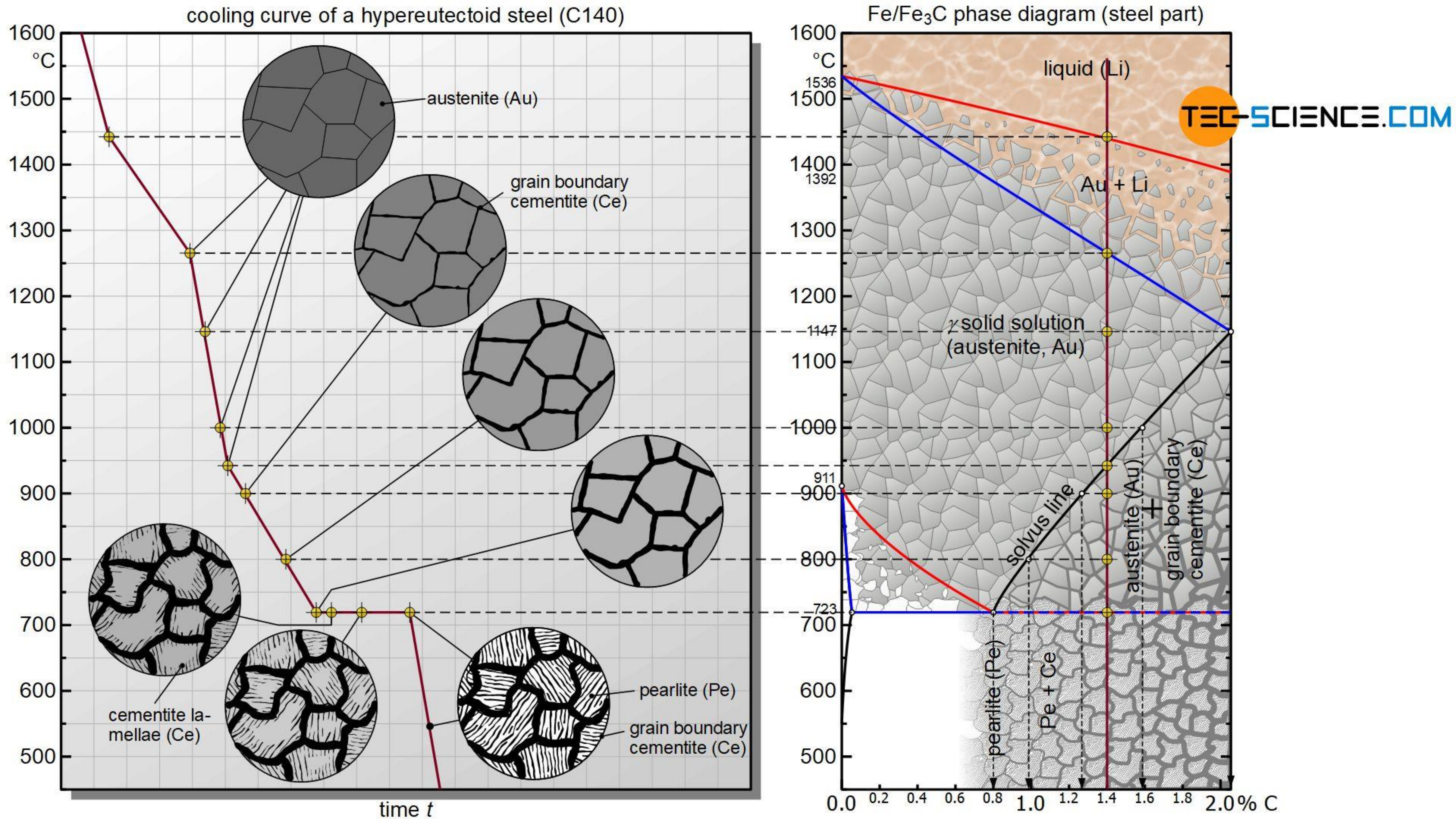


- Pearlite is a micro-constituent with alternating lamellae of cementite and ferrite.
- Pearlite is not a phase.






cooling curve of a hypoeutectoid steel (C40)
Fe/Fe3C phase diagram (steel part)
1600
°C
1500
1400
1300
1200
1100
1000
900
800
700
600
500
time t
austenite (Au)
ferrite (Fe)
cementite la-
mellae (Ce)
pearlite (Pe)
ferrite (Fe)
1536
1392
1147
911
723
liquid (Li)
Au + Li
γ solid solution
(austenite, Au)
ferrite (Fe)
+
austenite (Au)
solvus line
austenite (Au)
+
grain boundary
cementite (Ce)
Pe + Fe
pearlite (Pe)
Pe + Ce
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0 % C
TEC-SCIENCE.COM



cooling curve of a hypereutectoid steel (C140)
Fe/Fe3C phase diagram (steel part)
1600
°C
1500
1400
1300
1200
1100
1000
900
800
700
600
500
time t
austenite (Au)
grain boundary
cementite (Ce)
cementite la-
mellae (Ce)
pearlite (Pe)
grain boundary
cementite (Ce)
liquid (Li)
1536
1392
Au + Li
γ solid solution
(austenite, Au)
1147
911
723
solvus line
austenite (Au)
+
grain boundary
cementite (Ce)
pearlite (Pe)
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TEC-SCIENCE.COM
0.0
0.2
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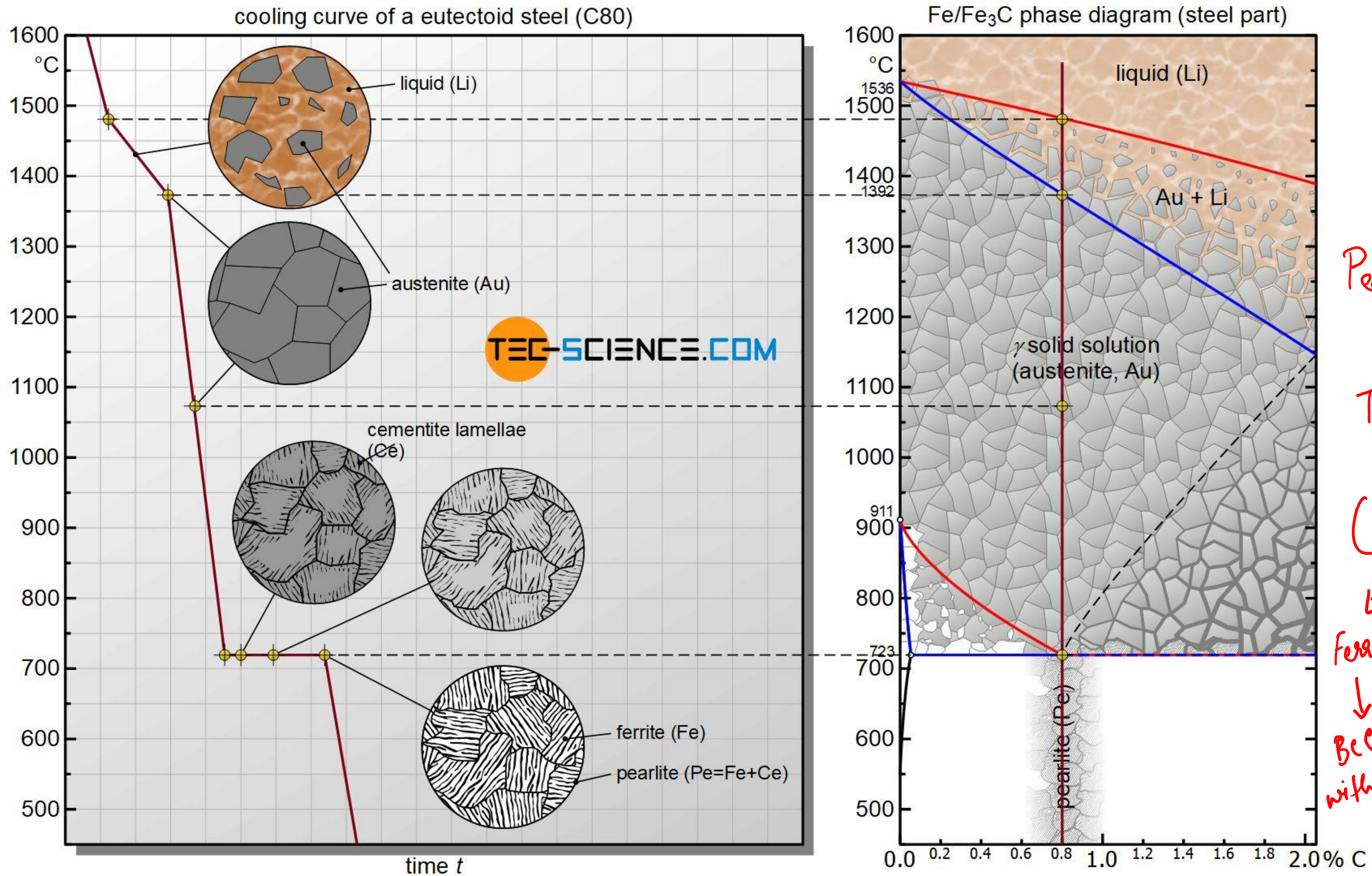
0.8
1.0
1.2
1.4
1.6
1.8
2.0 % C



Pearlite

⇓

Two-phase mixture

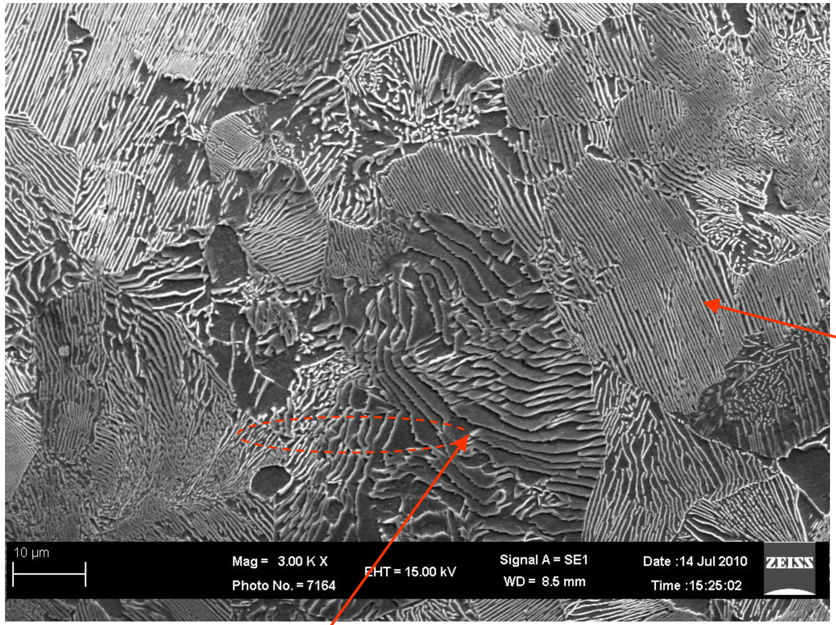
(α + Fe_3C)

Ferrite → Bcc-Fe with C-solubility

Cementite (Fe_3C)

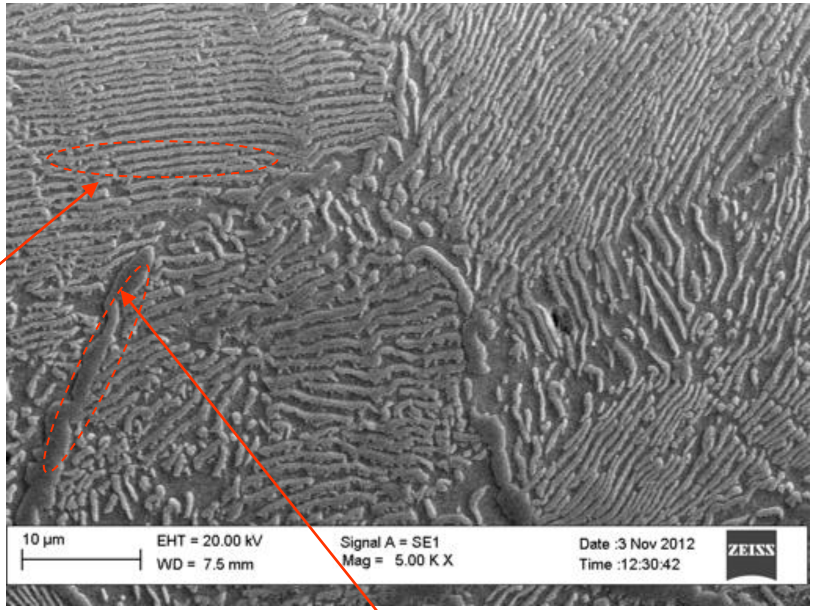
SEM micrograph of pearlite in eutectoid composition (0.8% C) of steel

SEM micrograph of pearlite in hypo-eutectoid composition (1% C) of steel



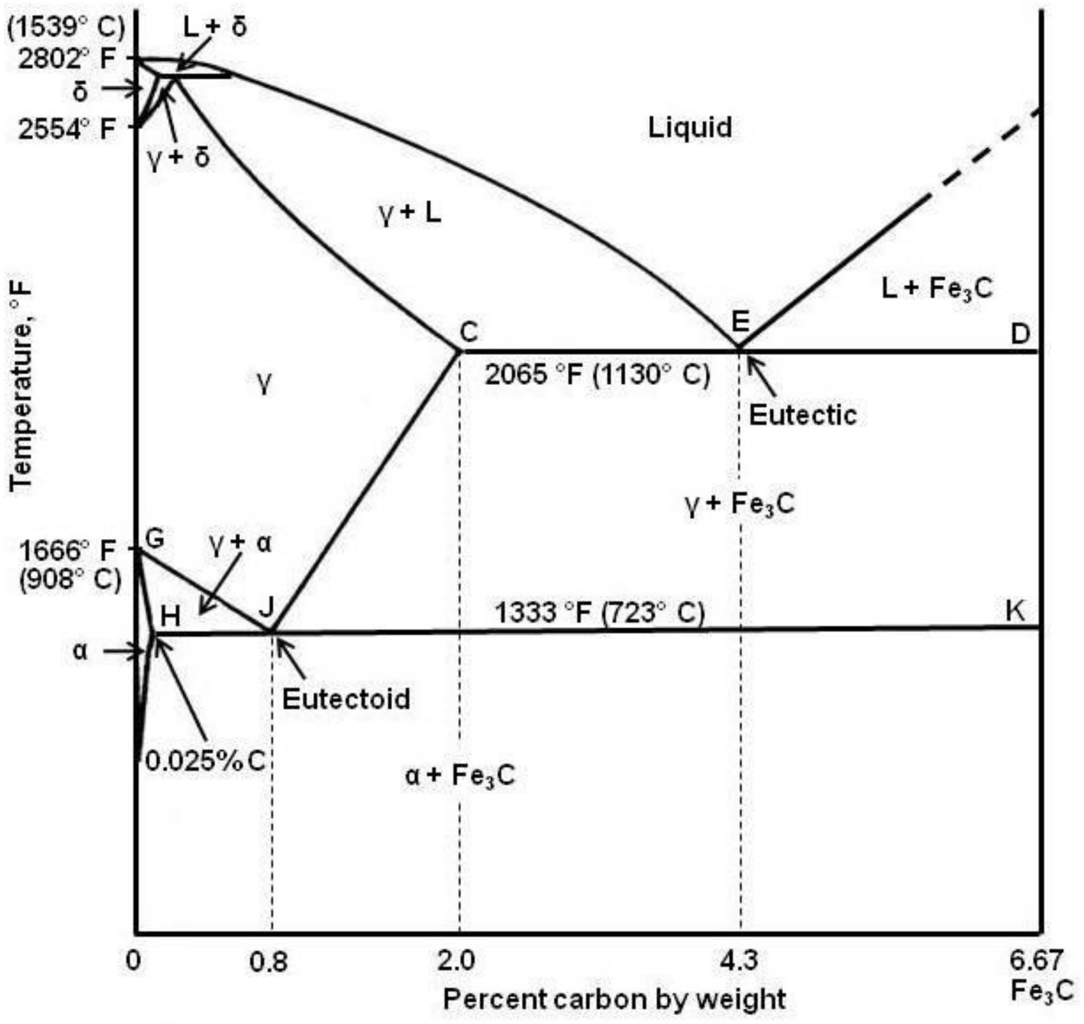
lamellar spacing in the micrograph: different orientation of the lamellae

Pearlite



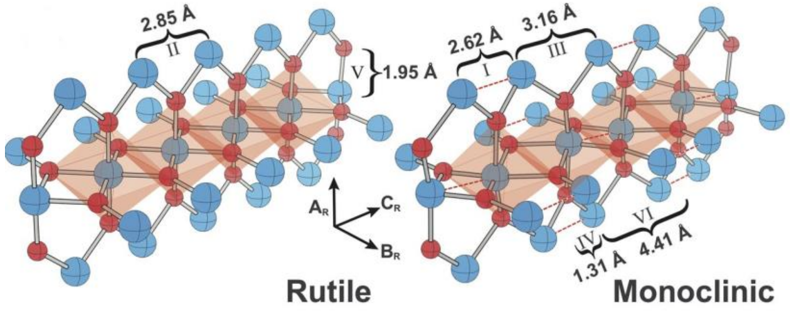
Pro-eutectoid Cementite along prior austenite grain boundaries

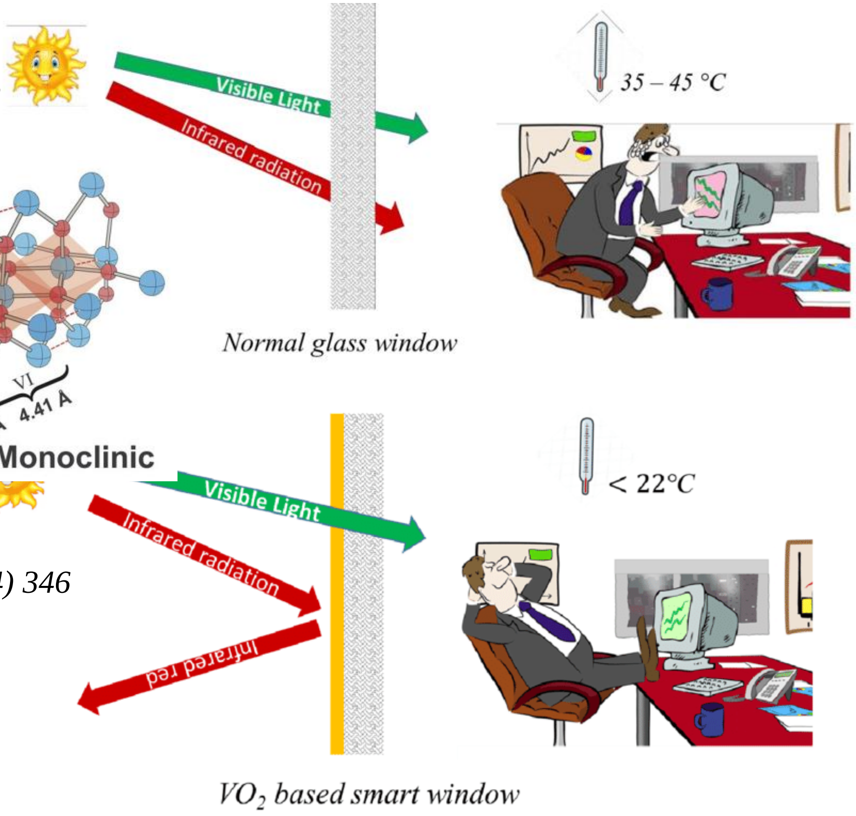
A steel contains 20% pearlite and 80% pro-eutectoid (primary) ferrite at room temperature. Is the steel hypoeutectoid or hypereutectoid?



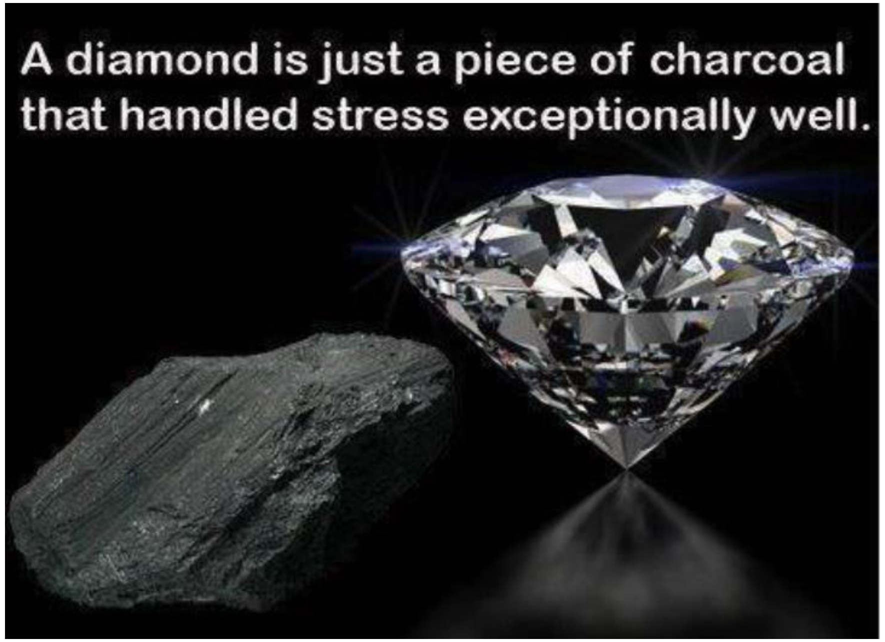
Phase Transformation

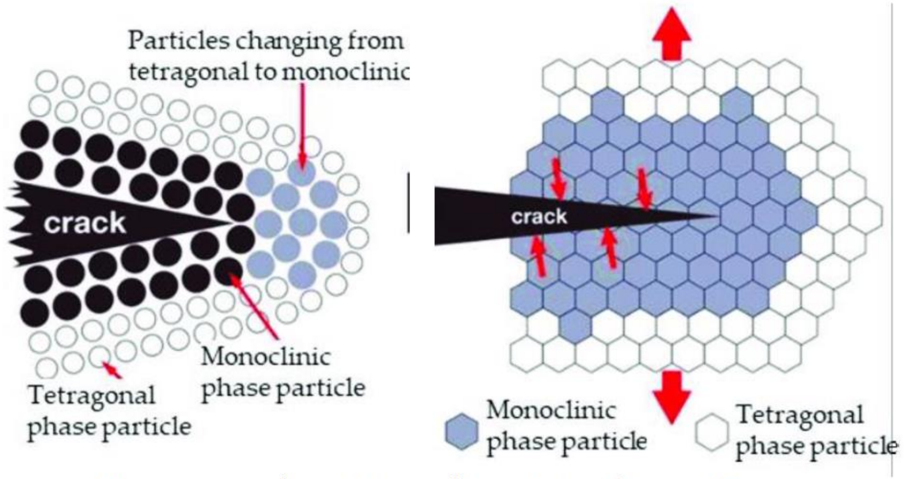
Smart windows





Morrison et al., Science (2014) 346





Stress can also cause phase transformation

Why should one learn phase transformation?

- What causes phase transformation? -----> Temperature and Pressure
- Knowledge about phase transformation will aid at designing the material.

Engineering of Microstructure and phase → Enhancement of desired properties in applications

MLL 100

Introduction to Materials Science and Engineering

Lecture-15 (February 09, 2022)

Dr. Sangeeta Santra (*ssantra@mse.iitd.ac.in*)

IIT Delhi
Department of Materials Science and Engineering

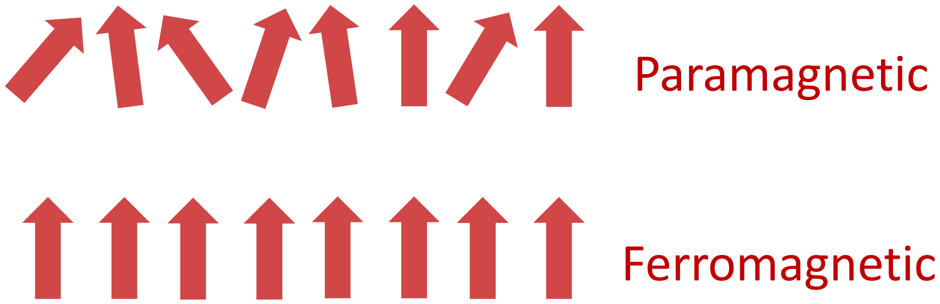
What have we learnt in Lecture-14?

- Radius ratio rule (Pauling’s rule) for ionic structure
- Pearlite

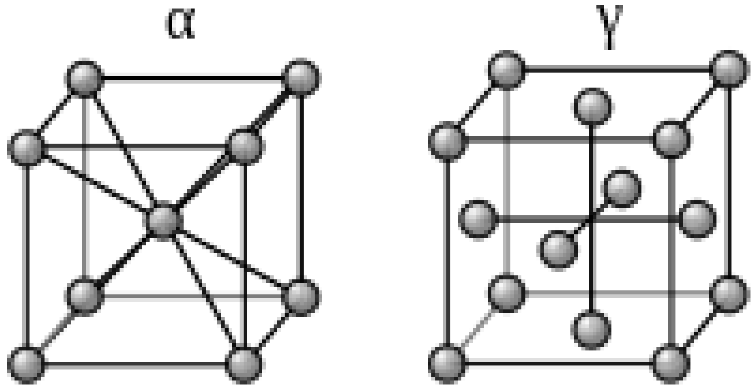
Phase transformation

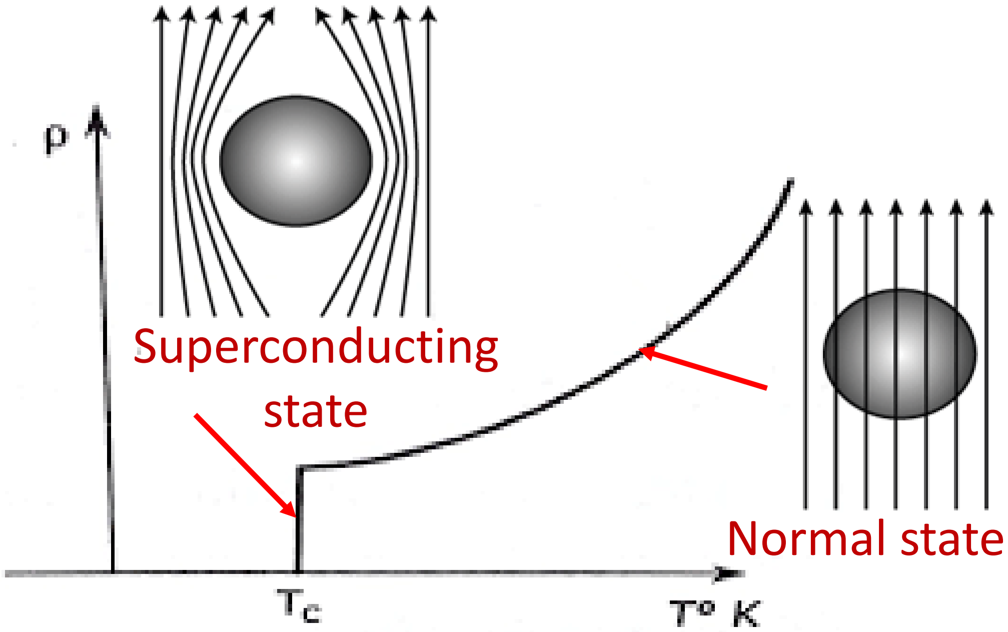
☞ **Change in 'state'**

☞ **Change in 'Property'**



☞ **Change in 'crystal structure'**

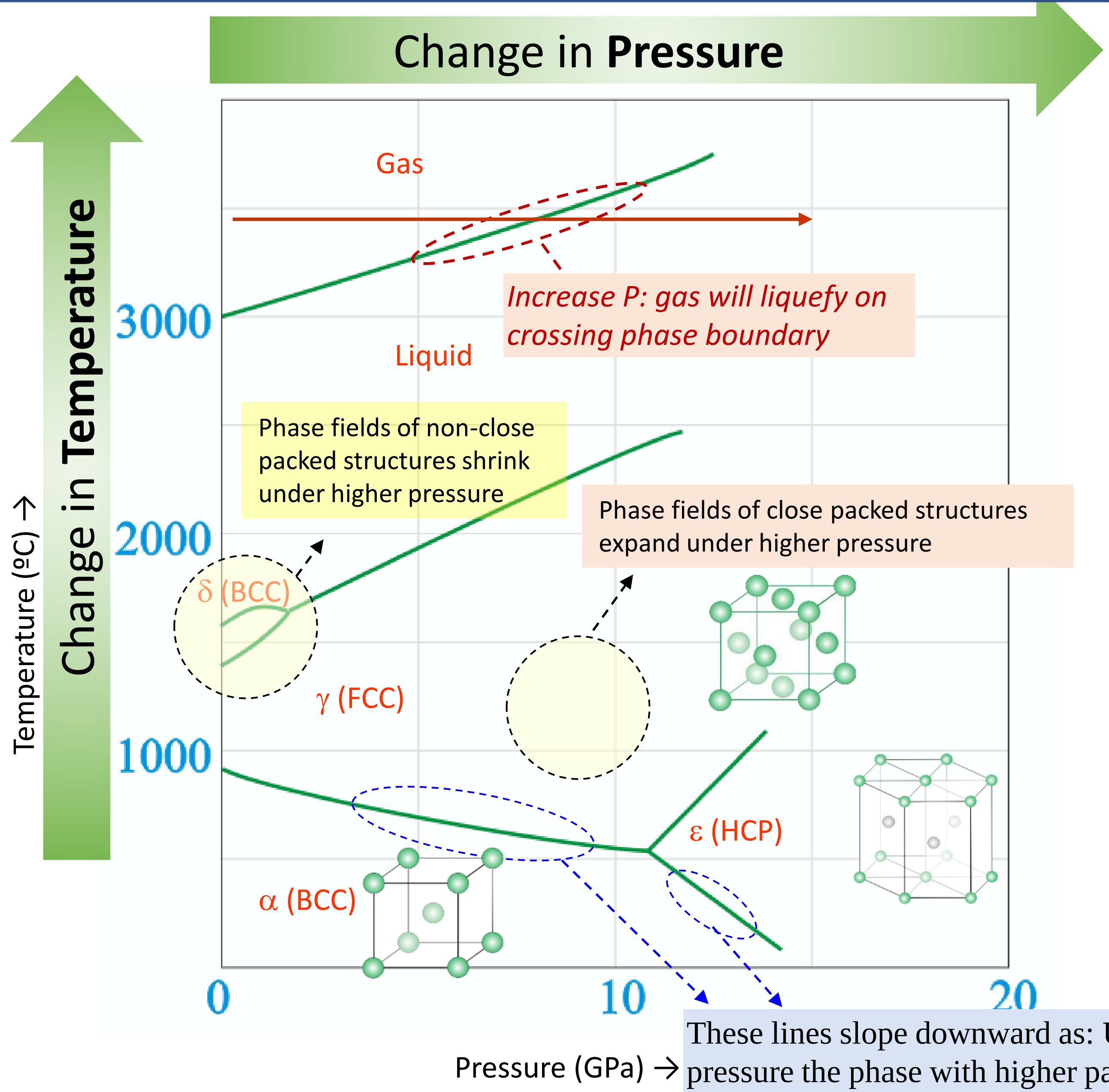




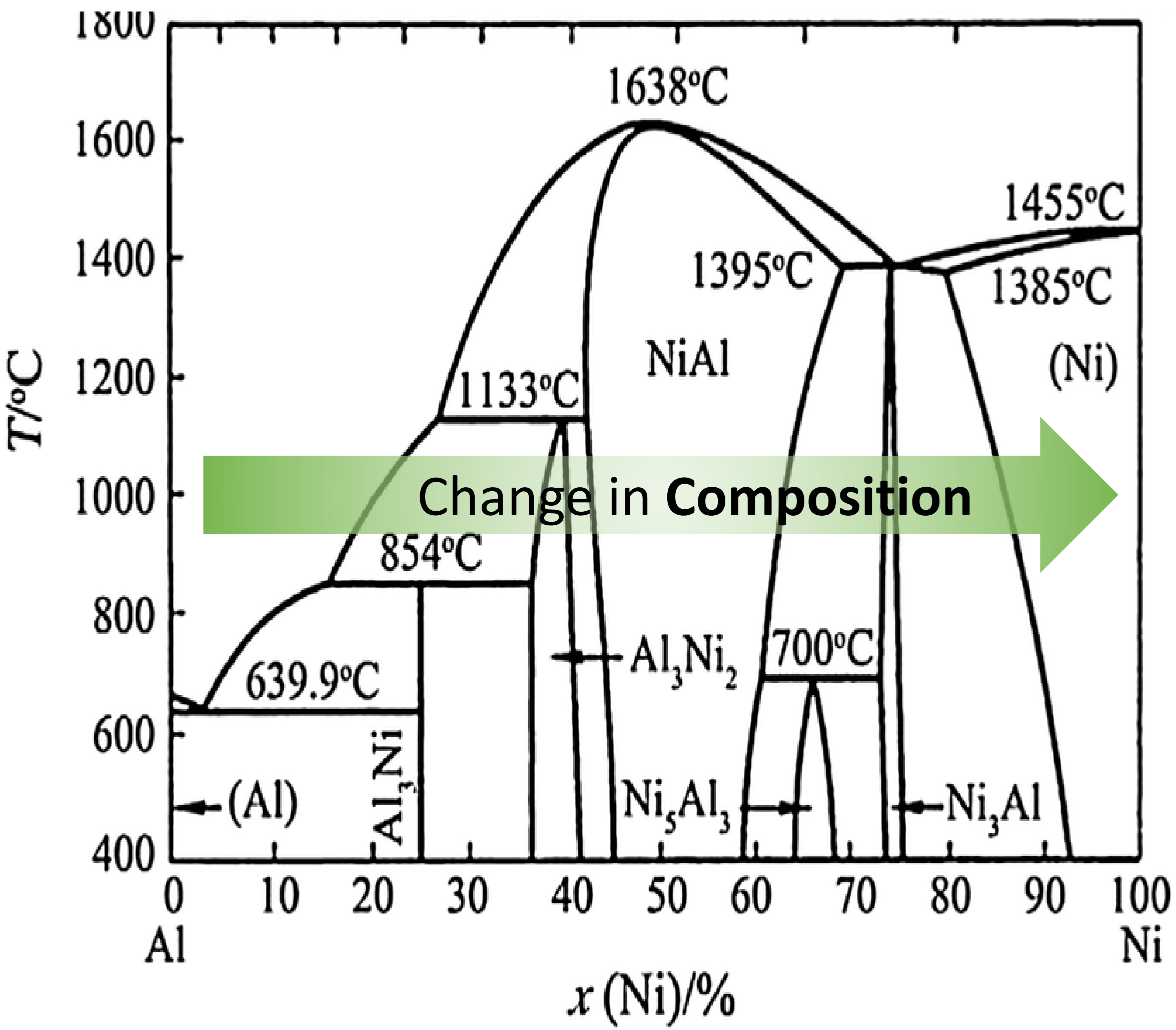
Transformation of one phase to another involving a change in chemical, structural, or physical properties caused by any external stimulus.

What could be those external stimuli?

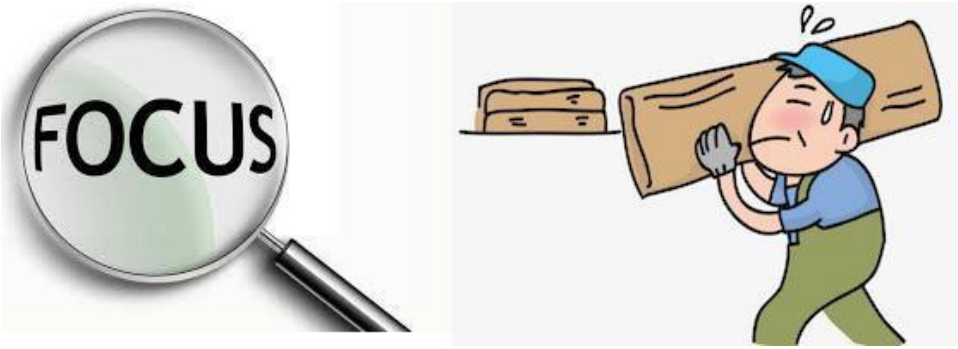
Factors aiding phase transformation



These lines slope downward as: Under higher pressure the phase with higher packing fraction (lower volume) is preferred



Why does 'Phase transformation' occur?



Very high motivation

When do you feel like transforming yourself?

↓

You are bit unhappy, or down ----> Not 'stable'

↓

Restless (**Unstable state**)

Working very hard

↓

Put an extra effort to transform yourself

↓

Saddle point

State after transformation

↓

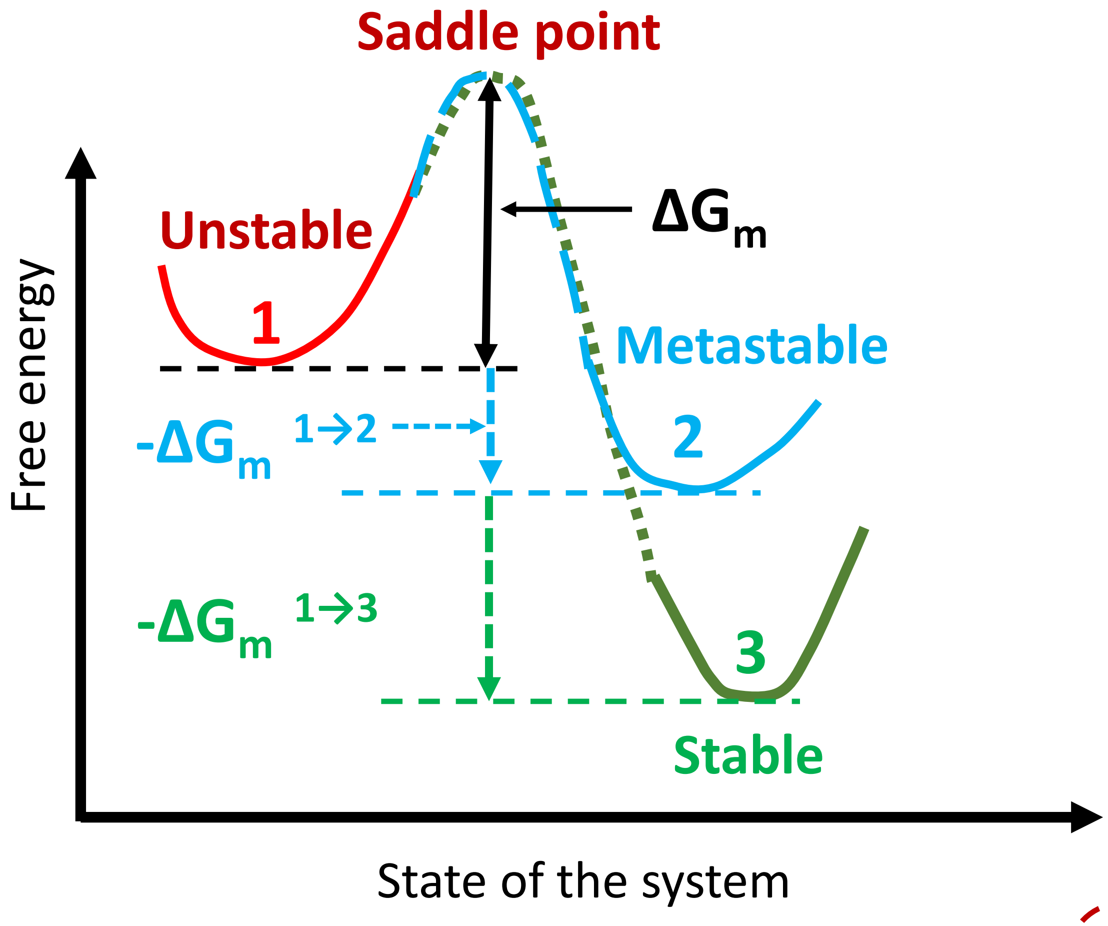
Stable state

Initial state of the system is 'unstable' relative to the final state of the system

When will the phase be called in an ‘unstable’ state?

Is it necessary for a transformation to reach the stable state directly from an unstable state?

How is stability of a system measured?



- Thermodynamic control involves lowering of Gibbs free energy, **G = G$_m$ (T, P, n)**

$$dG = -SdT + VdP + \sum_{i=1}^{N} \mu_i dN_i$$

$$\boxed{\left(\frac{dG}{dN_i}\right)_{T,P} = \mu_i}$$

Chemical potential

Does only 'Gibbs free energy' dictate the phase stability?

The dictating thermodynamic potential depends on the state variables which are held constant during the process.

On cooling just below T_m solid becomes stable, i.e. $G_{Liquid} > G_{solid}$

However, when we are just below T_m solidification does not 'start'.
E.g. liquid Ni can be undercooled 250 K below T_m.

Driving force for phase transformation

Liquid → Solid (α)

Thermodynamic driving force for a phase transformation?

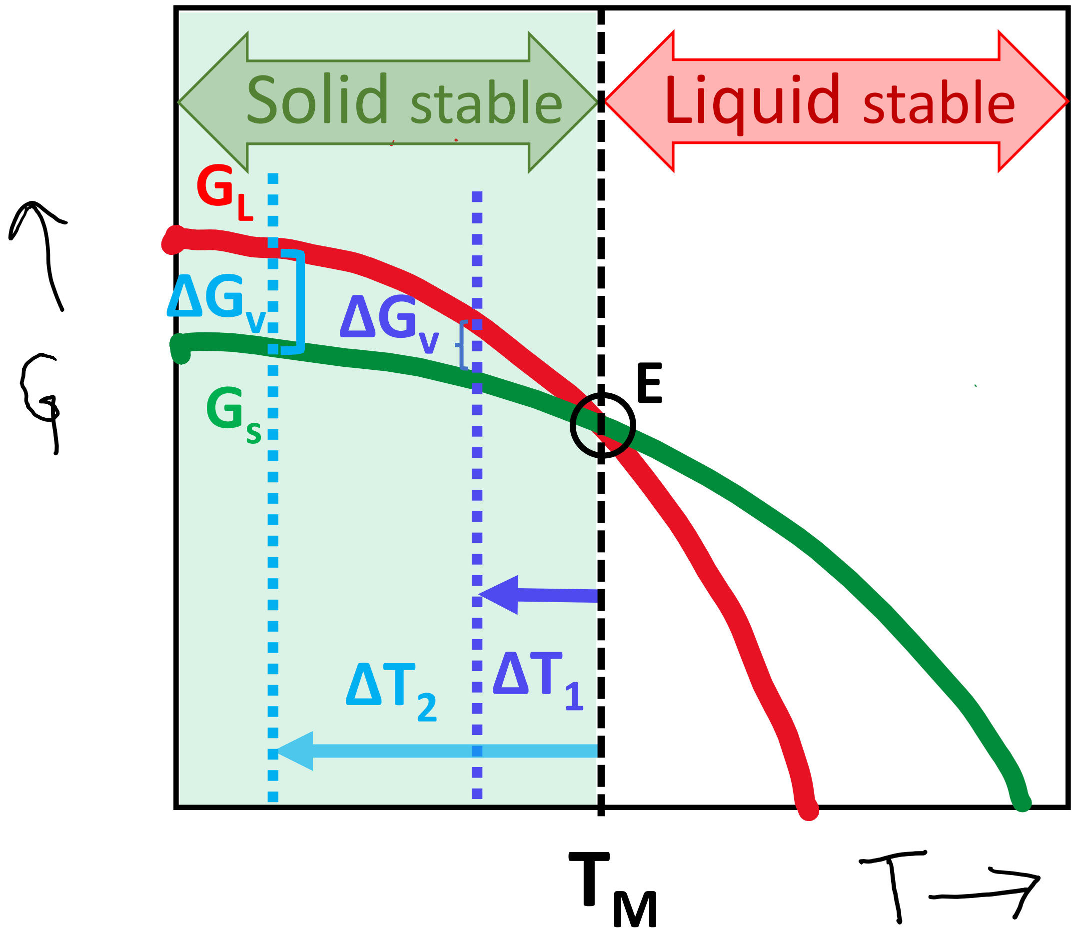
Decrease in Gibbs free energy

Liquid ---> solid

$G_s - G_l = \Delta G = -ve$

Lower the free energy, stable is the phase.

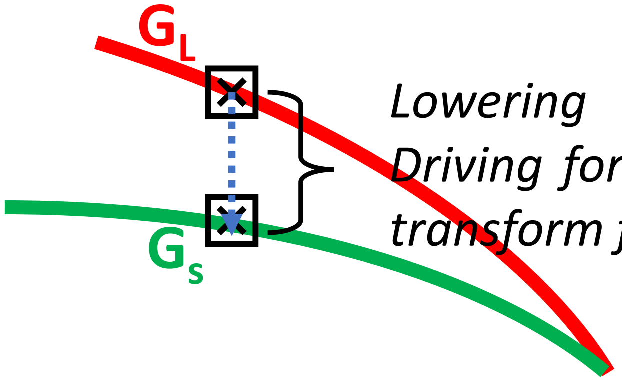
$\Delta G = (G_S - G_L) < 0$



- G_S: Free energy of solid
- G_L: Free energy of liquid

- At 'E', $G_S = G_L$

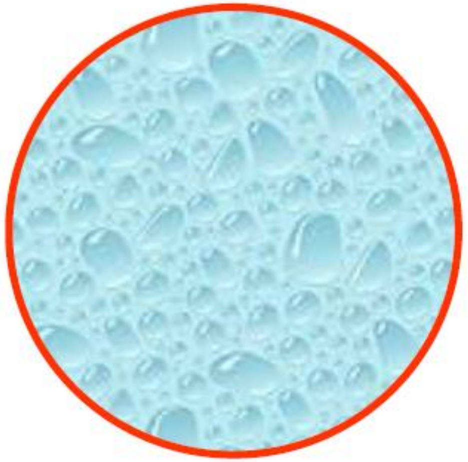
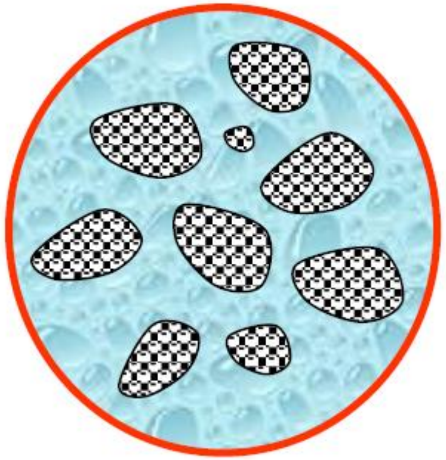
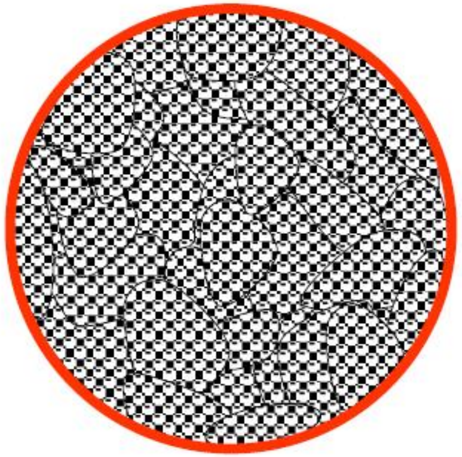
- ΔT : Undercooling or supercooling



Lowering of free energy: Driving force for the phase to transform from liquid to solid

❑ *When will the solid transform to the liquid?*

Mechanism (Steps) of a phase transformation

Solidification		**Nucleation** *of solid crystals from melt*		**Growth** *of nucleated crystals till liquid is exhausted*
	=		+	
		Formation of stable particles of solid		*Increase in size of the formed stable particles of solid*

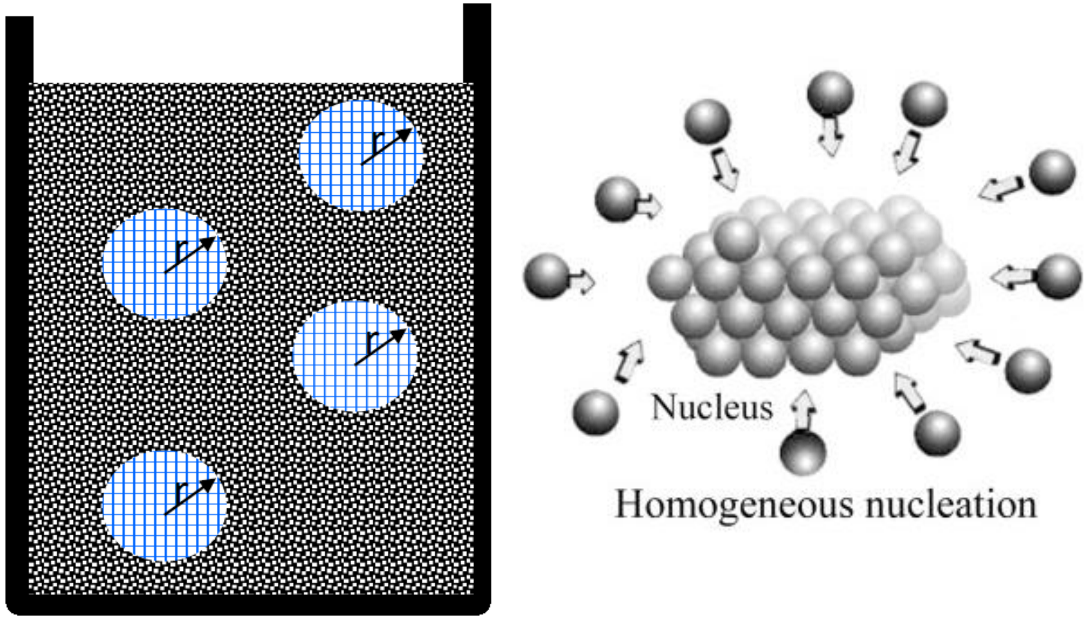
Nucleation

- Formation of a nucleus of a phase from a second phase (in general, for any kind of phase transformation).

- Formation of a solid nucleus from liquid phase (in particular, for solidification).

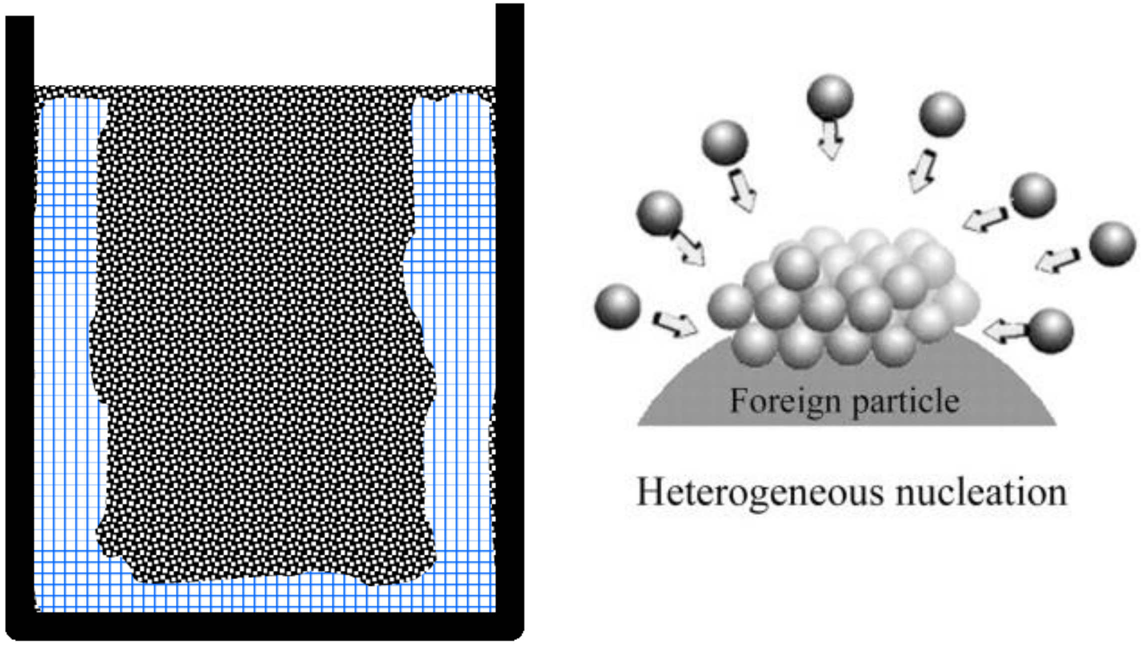
Types of Nucleation

Homogeneous Nucleation



Probability of nucleation occurring at any given site in volume of parent phase is identical to that any other site

Heterogeneous Nucleation

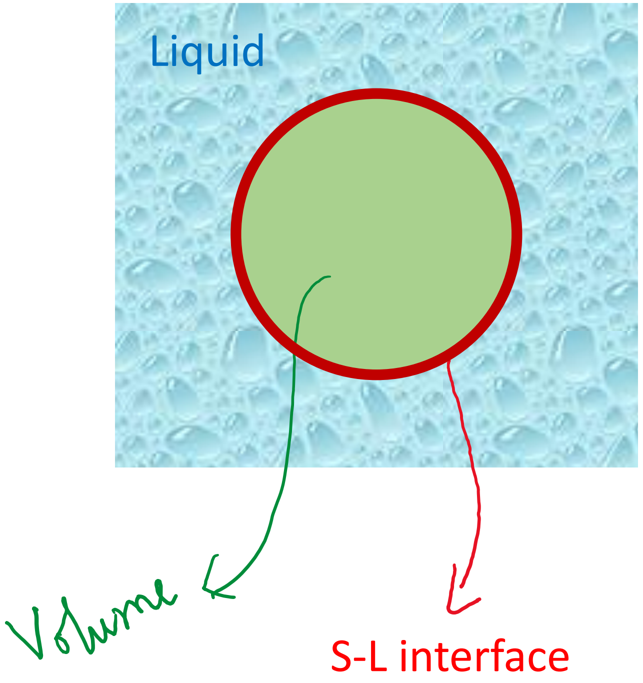


Probability of nucleation occurring at preferred site (e.g. grain boundaries, dislocations, inclusions, mould wall) is much more than that at any other site

Homogeneous nucleation

- Consider L$\rightarrow$S transformation taking place by homogenous nucleation.
- Let the system be undercooled to a fixed temperature.
- Let us consider the formation of a spherical crystal of radius ‘r’ from the melt.
- The change in ‘G’ during the process, if be, ΔG.

$T < T_M$



Total change in energy,

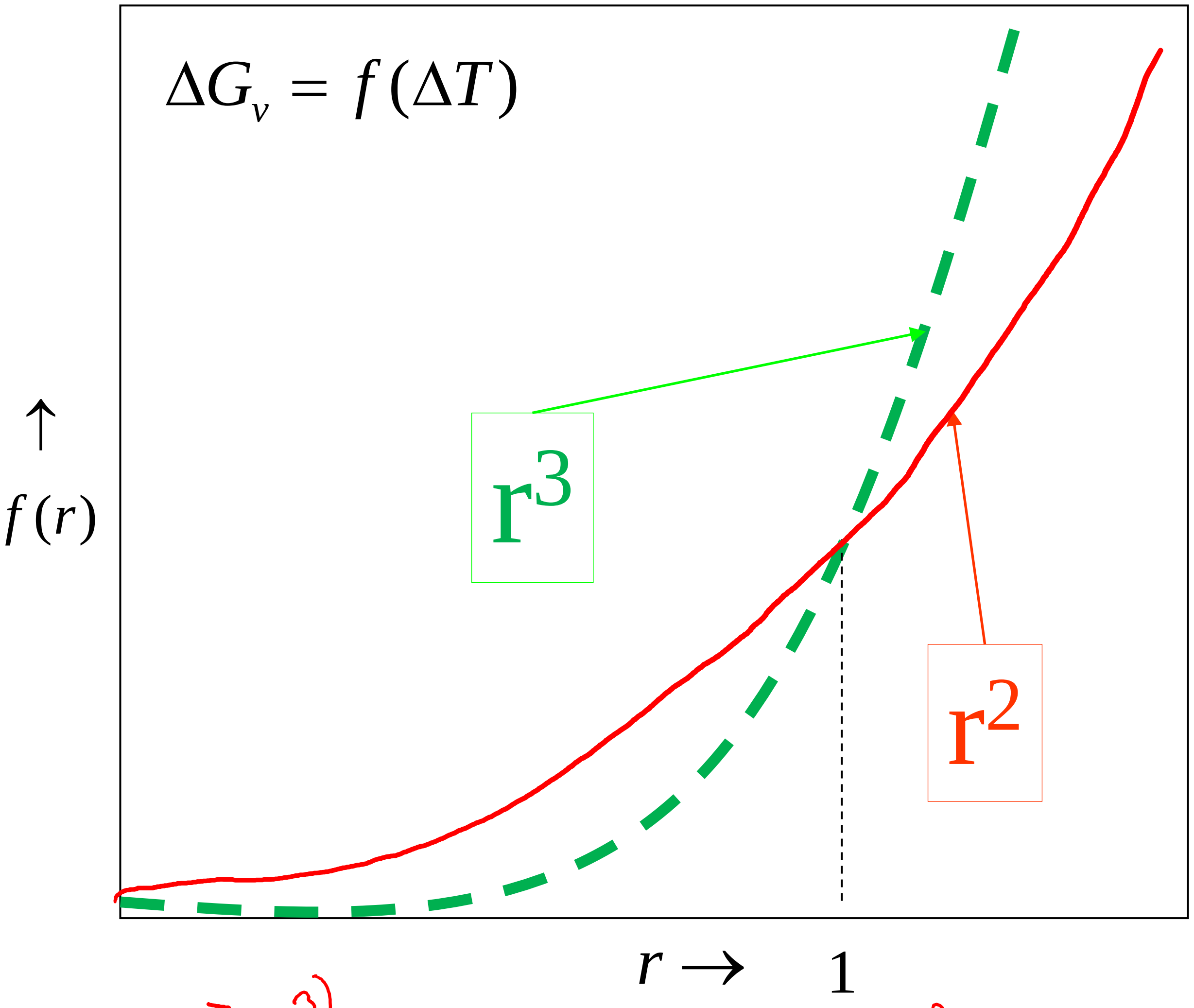
$$\Delta G = -(\boldsymbol{V}.\Delta \boldsymbol{G_v}) + (\boldsymbol{A}.\boldsymbol{\sigma_{sl}})$$

Transformation of a liquid portion to a solid portion with lower energy

Creation of an interface

Considering the nucleus to have a spherical shape with radius ‘r’:

$$\Delta G = -\left(\frac{4}{3}\pi r^3 \,.\, \Delta G_v\right) + (4\pi r^2 \,.\, \sigma_{sl})$$



$$\Delta G = -\left(\frac{4}{3}\pi r^3 \,.\, \Delta G_v\right) + \left(4\pi r^2 \,.\, \sigma_{sl}\right)$$

- Smaller radius (r) : 'r^2' term will be greater than 'r^3', therefore, the interfacial energy term will dominate the nucleation.

- Larger radius (r) : 'r^3' term will be greater than 'r^2', therefore, the volume free energy term will dominate the nucleation.

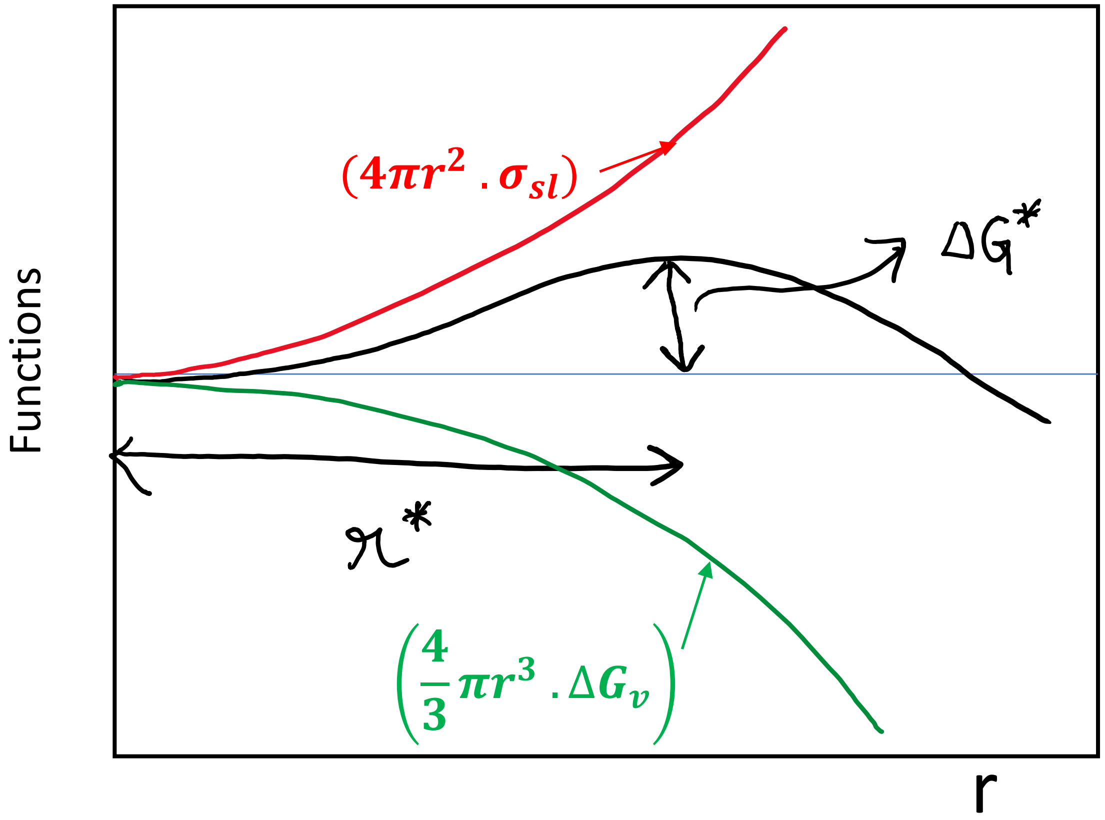
$(r^2 > r^3)$ $r = 0.1$ $r^2 = 0.01$, $r^3 = 0.001$

$(r^2 < r^3)$ $r = 10$ $r^2 = 100$, $r^3 = 1000$

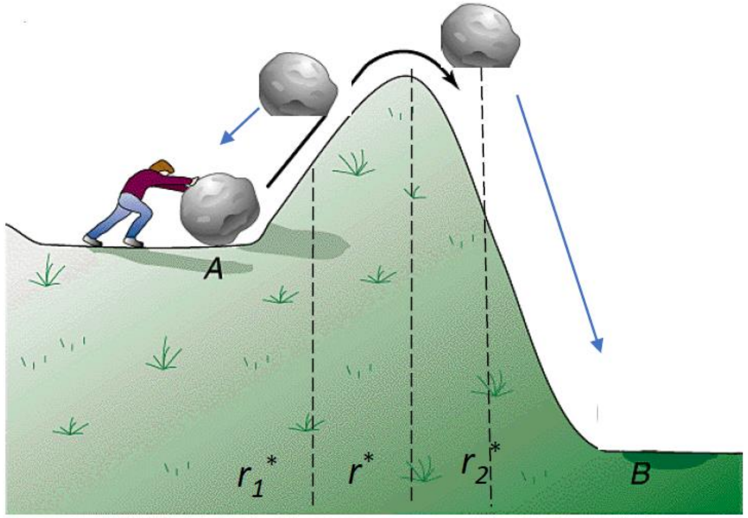
$$\Delta G = \underbrace{-\left(\frac{4}{3}\pi r^3 \,.\, \Delta G_v\right)}_{\text{supports } L \rightarrow S} \underbrace{+ \left(4\pi r^2 \,.\, \sigma_{sl}\right)}_{\text{Opposes } L \rightarrow S}$$

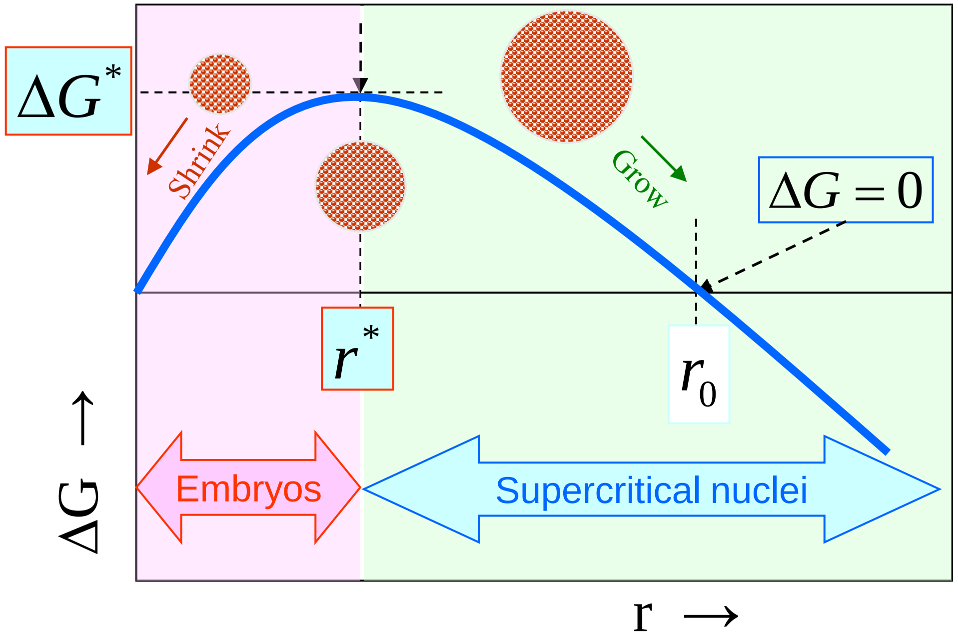
The energy which a system already has

Additional energy which a system needs to be supplied with



- There should be a minimum or maximum in the function of the free energy change for L → S.
- What governs that minimum/maximum? …. σ_{sl} and ΔG_v
- $f(\sigma_{sl}) \propto r^2$ and $f(\Delta G_v) \propto r^3$
- For lower limit of ‘r’, σ_{sl} dominates, and higher limit of ‘r’, ΔG_v dominates





- ΔG vs r plot goes through a maximum: 'G' increases when a small crystal forms and would tend to dissolve.

- Maximum of ΔG vs r plot is obtained by by setting dΔG/dr = 0. The maximum value of ΔG corresponds to a value of 'r' called the critical radius (r^*).

- If because of some *'statistical random fluctuation'* a crystal of 'preferred' crystal structure with size > r* *(called supercritical nuclei)* forms, then it can grow because of a favourable 'G' trend. Crystals smaller than r* *(called embryos)* will tend to shrink to reduce 'G'. The critical value of ΔG at r* is called ΔG*.

- Reduction in G (below the liquid state) is obtained only after r_0 is obtained (which can be obtained by setting ΔG = 0).

What is that minimum/maximum?:

$$\frac{d\Delta G}{dr} = -\left(4\pi r^2 . \Delta G_v\right) + \left(8\pi r . \sigma_{sl}\right)$$

$$\frac{d}{dr}\left(\frac{4}{3}\pi r^3\right)$$

$$\frac{4}{3} \times 3 . \pi r^2$$

At either minimum/maximum:

$$\frac{d\Delta G}{dr} = 0 \qquad 0 = -\left(4\pi r^2 . \Delta G_v\right) + \left(8\pi r . \sigma_{sl}\right)$$

$$\boxed{r^* = \frac{2\sigma_{sl}}{\Delta G_v}}$$

Critical nucleus size

$$\left(4\pi r^2 . \Delta G_v\right) = \left(8\pi r . \sigma_{sl}\right)$$

The change in free energy for the critical nucleus size:

$$\Delta G = -\left(\frac{4}{3}\pi r^3 . \Delta G_v\right) + \left(4\pi r^2 . \sigma_{sl}\right)$$

$$= -\left[\frac{4}{3}\pi\left(\frac{2\sigma}{\Delta G_v}\right)^3 . \Delta G_v\right] + \left[4\pi\left(\frac{2\sigma}{\Delta G_v}\right)^2 . \sigma_{sl}\right]$$

$$= -\left(\frac{4}{3}\pi . \frac{8\sigma^3}{\Delta G_v^3} . \Delta G_v\right) + \left(4\pi . \frac{4\sigma^2}{\Delta G_v^2} . \sigma_{sl}\right)$$

$$= \frac{-8\pi\sigma^3}{\Delta G_v^2}\left(\frac{4}{3} - 2\right) = \boxed{\frac{16\pi\sigma^3}{3\Delta G_v^2} = \Delta G^*}$$

2nd Quiz of MLL100

- Date: 12-02-2022 (Saturday)
- Time: 10:30 am – 10:45 am
- Duration: 15 minutes
- Via: Moodle
- Question type: Multiple-choice
- Negative marking: No
- Navigation: Sequential
- Syllabus: Phase diagram, equilibria and transformation

Minor exam of MLL100

- Date: 16-02-2022 (Wednesday)
- Time: 3:45 pm – 4:45 pm
- Duration: 1 h
- Via: Moodle
- Question type: Multiple-choice
- Negative marking: Yes
- Navigation: Off
- Syllabus: Content covered until 12-02-2022

MLL 100

Introduction to Materials Science and Engineering

Lecture-16 (February 11, 2022)

Dr. Sangeeta Santra (*ssantra@mse.iitd.ac.in*)

IIT Delhi
Department of Materials Science and Engineering

What have we learnt in Lecture-15?

- ❑ Steps involved in Phase transformation
- ❑ Gibb’s free energy
- ❑ Chemical potential
- ❑ Types of nucleation
- ❑ Critical radius and critical free energy of homogeneous nucleation

Variation of r* and ΔG* with undercooling

Critical nucleus size, $r^* = \frac{2.\gamma_{sl}}{\Delta G_v}$

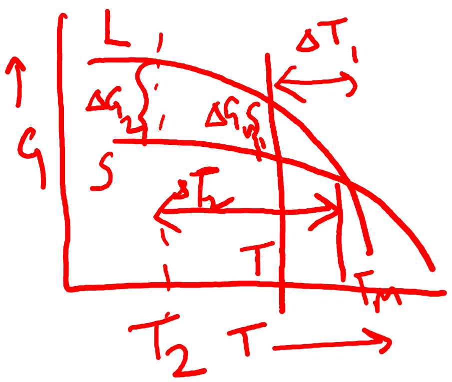
$$r^* = \frac{2.\gamma_{sl} T_m}{L.\Delta T}$$

Free energy change for a nucleus with critical size,

$$\Delta G^* = \frac{16\pi\gamma_{sl}^3}{3.(\Delta G_v)^2}$$

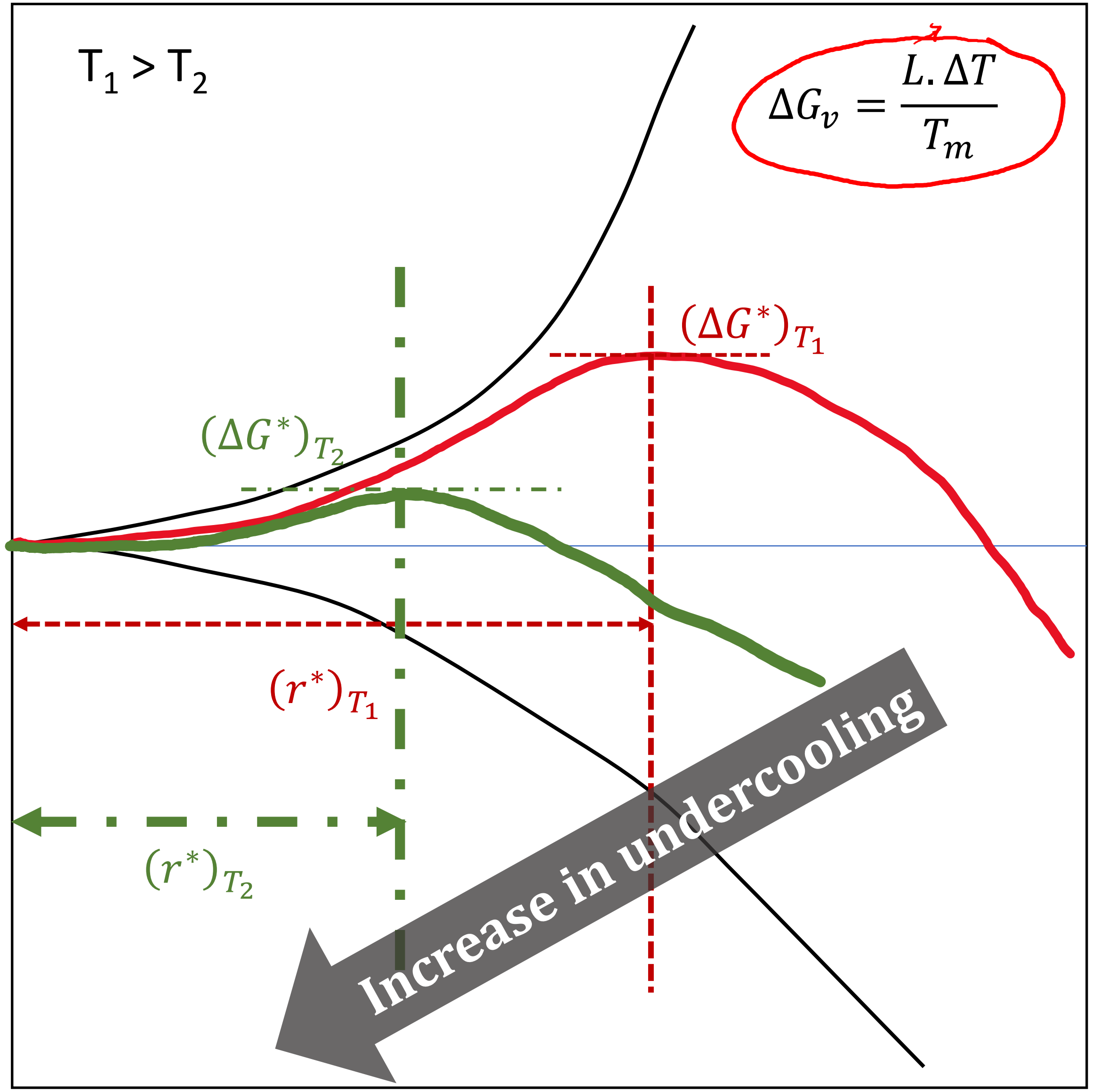
$$\Delta G^* = \frac{16\pi\gamma_{sl}^3 T_m^2}{3.L^2(\Delta T)^2}$$

$\Delta T \uparrow \quad \Delta G_v \uparrow$



$$\Delta G_v = \frac{L.\Delta T}{T_m}$$

$G = H - TS$



Both the 'critical nucleus size' and the 'free energy required to form that critical nucleus' ***decrease with undercooling***.

$$\boxed{\Delta G = \Delta H - T\Delta S} \quad \text{—(1)}$$

$G \Rightarrow$ Gibb's free energy

$H \Rightarrow$ Enthalpy

$T \Rightarrow$ Temperature

$S \Rightarrow$ Entropy

At $T = T_M$, $G = 0$

$(\because G_S = G_L)$

$$\therefore \Delta G = 0 = (\Delta H - T_M \Delta S)$$

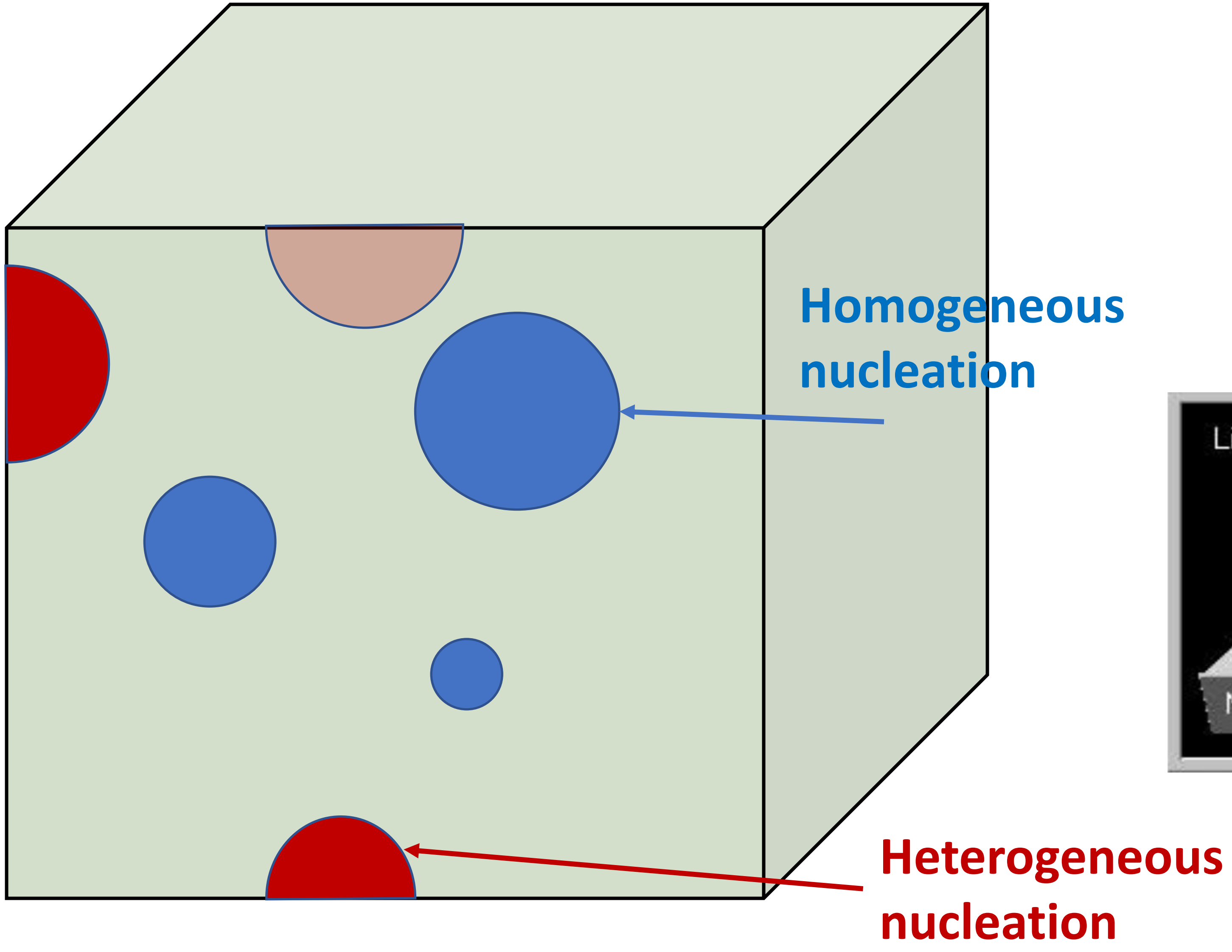
At $T = T_M$, $H =$ Latent heat (L)

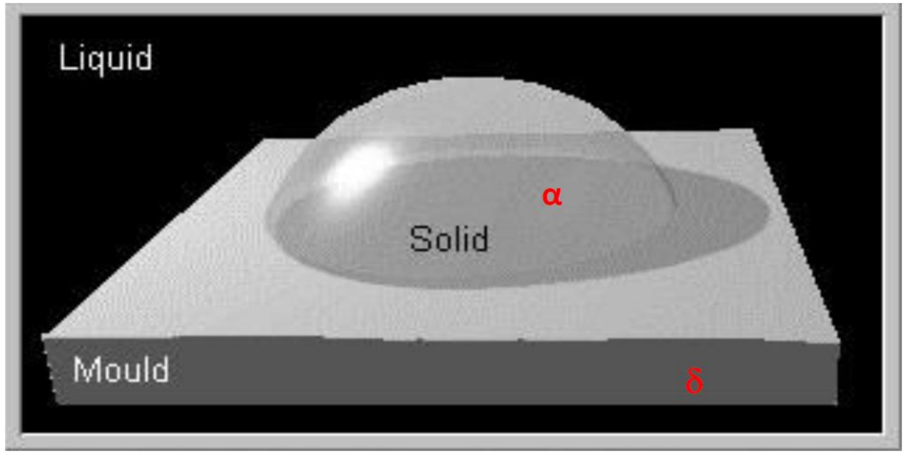
$$\therefore L = T_M S \quad \therefore S = \left(\frac{L}{T_M}\right) \quad \text{—(2)}$$

Substitute (2) in (1):

$$\Delta G = L - T\left(\frac{L}{T_M}\right) = L\left[1 - \frac{T}{T_M}\right] = L\left[\frac{T_M - T}{T_M}\right] = \left(\frac{L \cdot \Delta T}{T_M}\right)$$

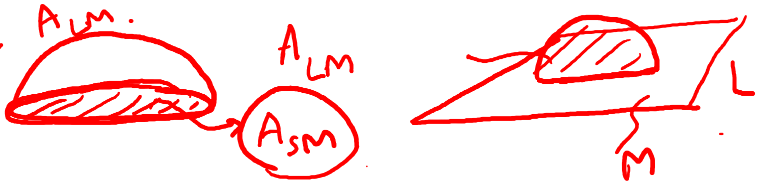
Heterogeneous nucleation





$$\Delta G_{het} = -V_s \Delta G_v + A_{SL}\gamma_{SL} + A_{SM}\gamma_{SM} - A_{LM}\gamma_{LM}$$

Earlier A_{LM}

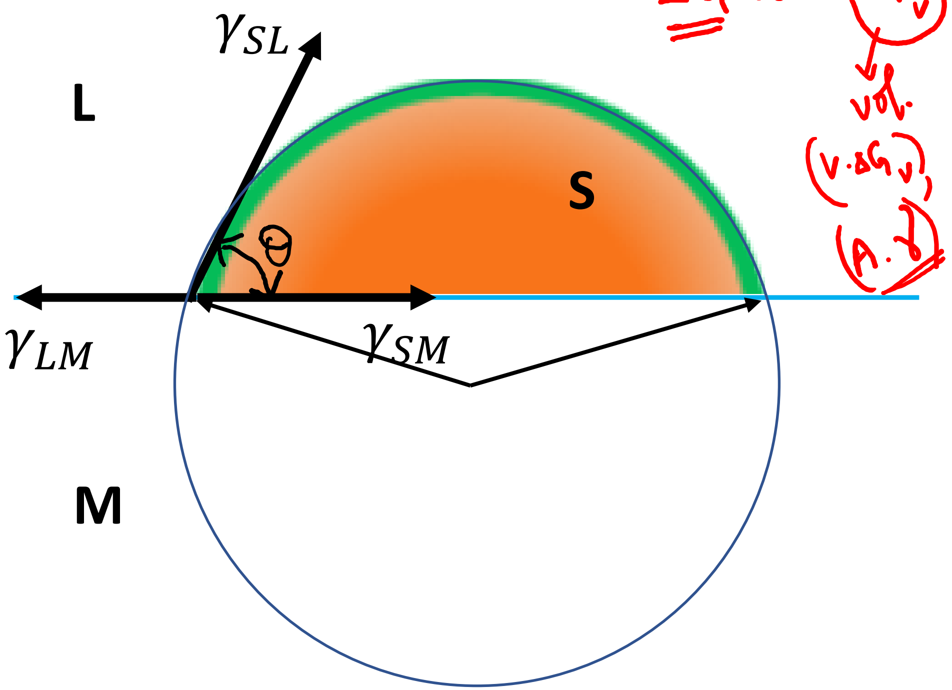


$\Delta G \propto \Delta G_v, \gamma$

vol.

$(V \cdot \Delta G_v)$

$(A \cdot \gamma)$



- Consider a solid nucleus (S) (of cap-shaped) on a mould (M) surface forming from liquid (L).

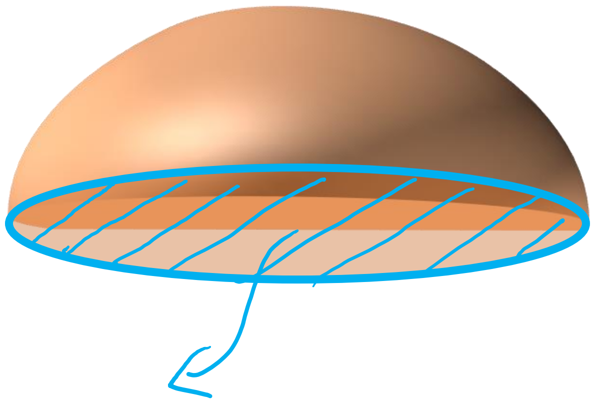
- Free energy associated with the heterogeneously nucleated solid particle,

$$\Delta G_{het} = -V_S \Delta G_v + A_{SL}\gamma_{SL} + A_{SM}\gamma_{SM} - A_{SM}\gamma_{LM}$$

Surface tension force balance parallel to the mould surface

$$\gamma_{LM} = \gamma_{SM} + \gamma_{SL} . \cos\theta$$

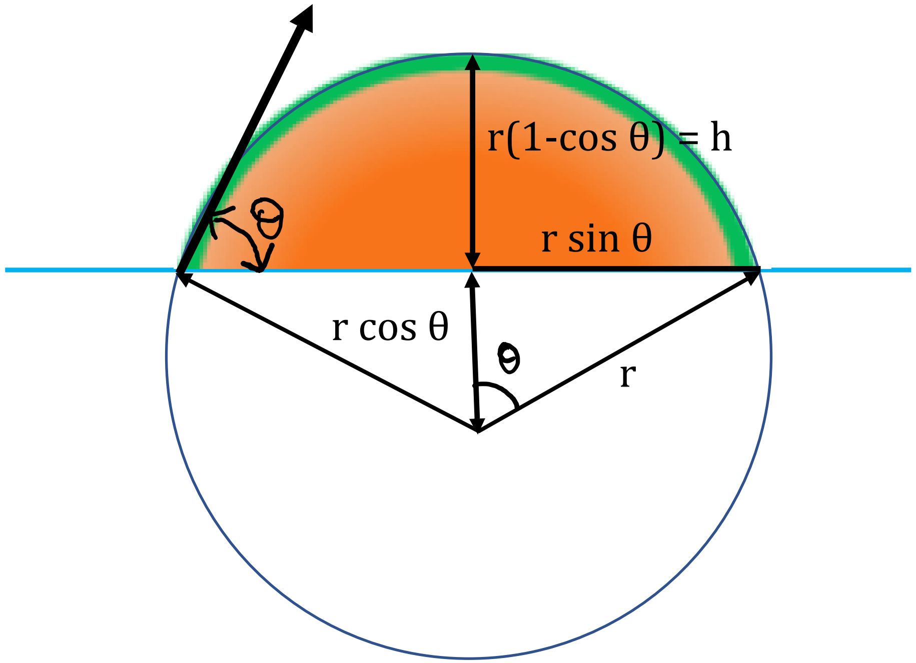
$$\cos\theta = \frac{(\gamma_{LM} - \gamma_{SM})}{\gamma_{SL}}$$



Creation of A_{SM}

Destruction of A_{LM}

$$\Delta G_{het} = -V_S \Delta G_v + A_{SL}\gamma_{SL} + A_{SM}(\gamma_{SM} - \gamma_{LM})$$



- Area of solid-liquid interface:

$$\begin{aligned} A_{SL} &= 2.\pi.r.h \\ &= 2.\pi.r.(r - r\cos\theta) \\ &= 2.\pi.r^2.(1-\cos\theta) \end{aligned}$$

- Area of solid-mould interface:

$$A_{SM} = \pi(r\sin\theta)^2$$

- Volume of the solid nucleus cap:

$$V = \frac{\pi}{6}h\left(3r^2 + h^2\right)$$

$$= \frac{\pi}{3}r^3\left(2 - 3\cos\theta + cos^3\theta\right)$$

- Substitution of these values in:

$$\Delta G_{het} = -V_S\Delta G_v + A_{SL}\gamma_{SL} + A_{SM}(\gamma_{SM} - \gamma_{LM})$$

$$\cos\theta = \frac{(\gamma_{LM} - \gamma_{SM})}{\gamma_{SL}}$$

- Re-arranging the terms in:

$$\Delta G_{het} = -\frac{4}{3}\pi r^3 \Delta G_v \left(\frac{2 - 3\cos\theta + cos^3\theta}{4}\right) + 4\pi r^2 \gamma_{SL}\left(\frac{2 - 3\cos\theta + cos^3\theta}{4}\right)$$

- Simplifying by taking the shape factor in common:

$$\Delta G_{het} = [-\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma_{SL}]\left(\frac{2 - 3\cos\theta + cos^3\theta}{4}\right)$$

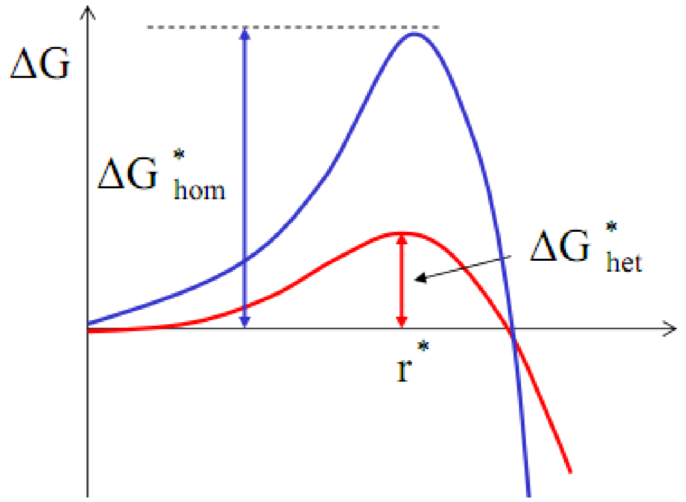
- The relation between free energy change for heterogeneous and homogeneous nucleation:

$$\Delta G_{het} = [\Delta G_{hom}]\left(\frac{2 - 3\cos\theta + cos^3\theta}{4}\right)$$

$$\frac{\Delta G_{het}}{\Delta G_{hom}} = \left(\frac{2 - 3\cos\theta + cos^3\theta}{4}\right)$$

- Free energy change at critical nucleus size for heterogeneous nucleation:

$$\Delta G^*_{het} = \frac{4\pi\gamma_{SL}^3}{3(\Delta G_v)^2}(2 - 3\cos\theta + cos^3\theta)$$



- Free energy change at critical nucleus size for heterogeneous nucleation:

$$\Delta G^*_{het} = \frac{4\pi\gamma_{SL}^3}{3(\Delta G_v)^2}(2 - 3\cos\theta + cos^3\theta)$$

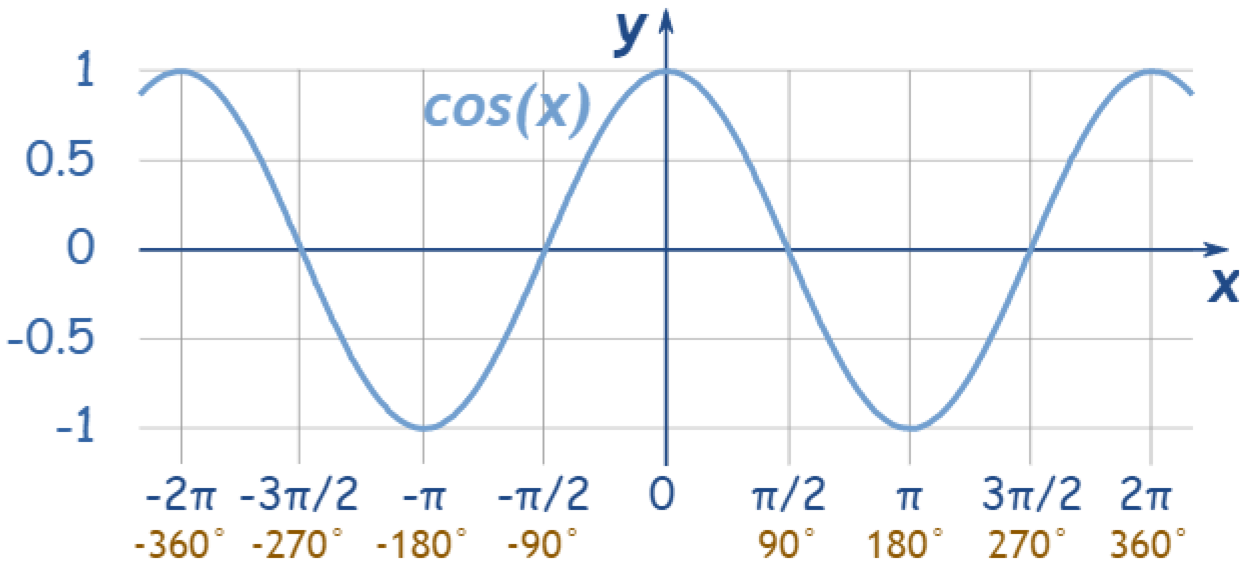
- Free energy change at critical nucleus size for homogeneous nucleation:

$$\Delta G^*_{hom} = \frac{16\pi\gamma_{SL}^3}{3(\Delta G_v)^2}$$

How can you relate the free energy changes for homogeneous and heterogeneous nucleation?

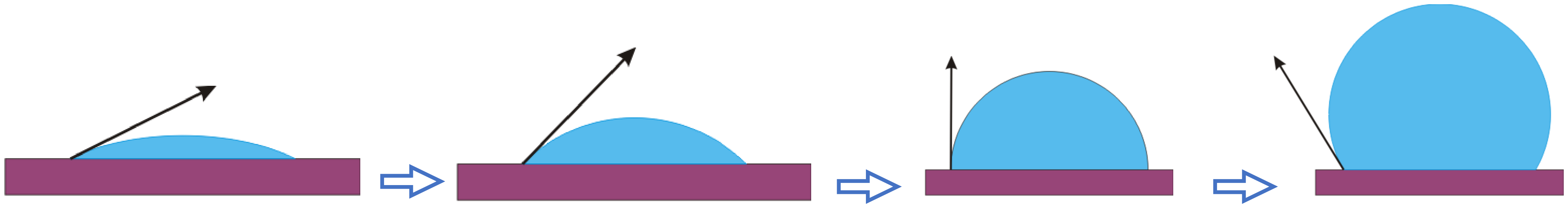
$$\Delta G^*_{het} = \frac{(\Delta G^*_{hom})}{4}(2 - 3\cos\theta + cos^3\theta)$$

$$\frac{\Delta G_{het}}{\Delta G_{hom}} = \left(\frac{2 - 3\cos\theta + cos^3\theta}{4}\right)$$



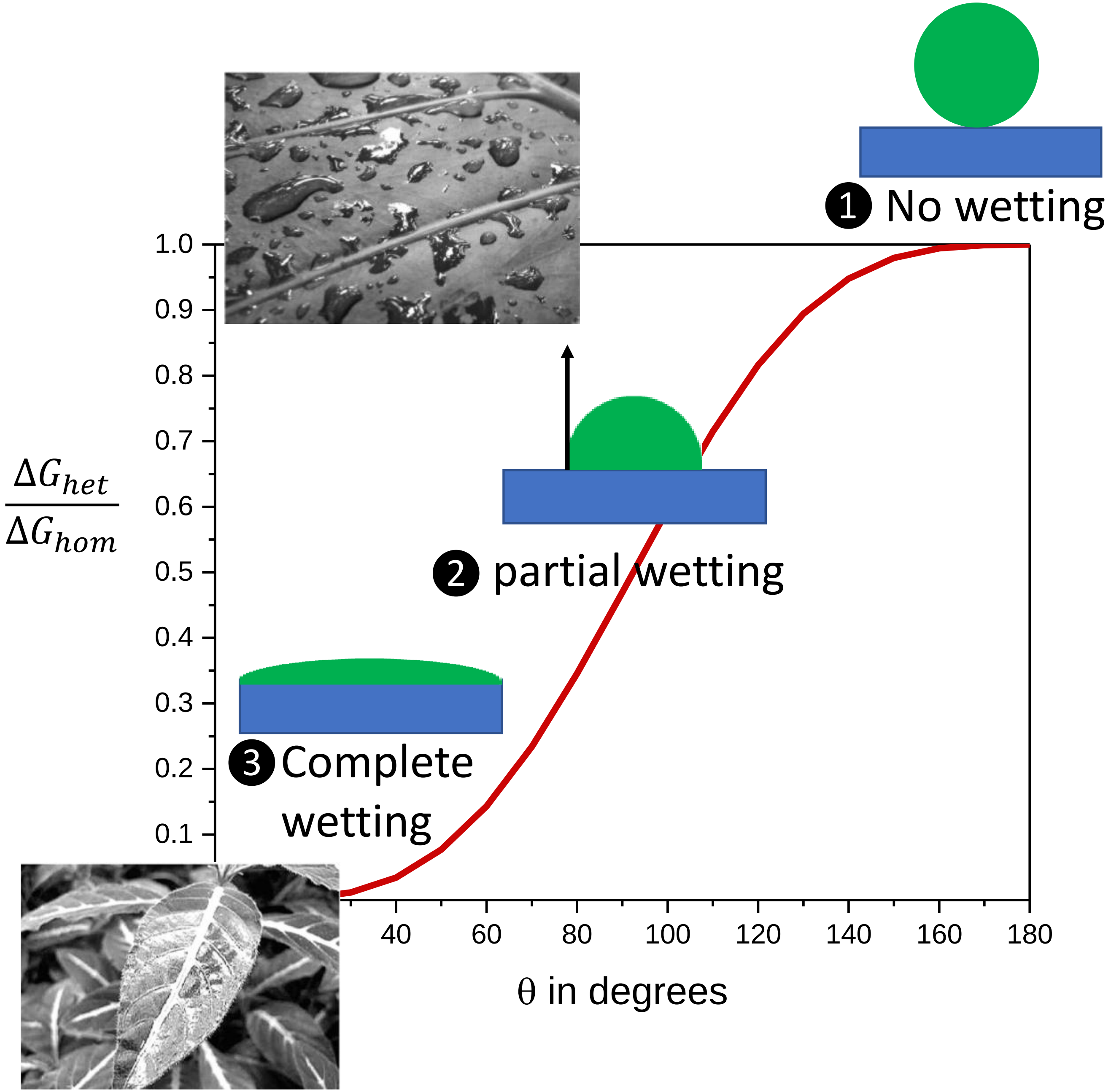
$$\Delta G^*_{het} = \frac{4\pi\gamma_{SL}^3}{3(\Delta G_v)^2}\left(2 - 3\cos\theta + cos^3\theta\right)$$

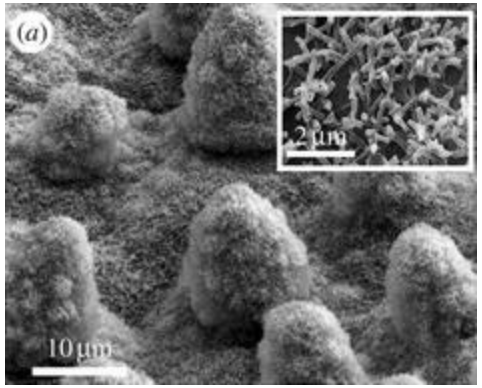
What happens when contact angle (θ) increases?



Tendency to wet the surface decreases

Wetting behaviour





$$\frac{\Delta G_{het}}{\Delta G_{hom}} = \left(\frac{2 - 3\cos\theta + \cos^3\theta}{4}\right)$$

❶ θ = 180° : ΔG_{het} = ΔG_{hom}, such a surface does not favour heterogeneous nucleation.

❷ θ = 90° : ΔG_{het} = 0.5 ΔG_{hom}, energy barrier for heterogeneous nucleation is half of the homogeneous one.

❸ θ = 0° : ΔG_{het} = 0, no energy barrier for heterogeneous nucleation.

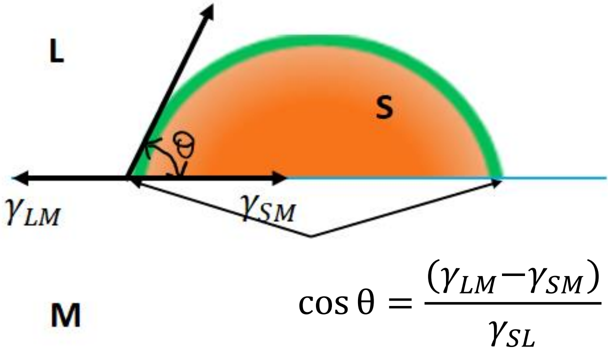
Selection of 'heterogeneous nucleation site'

❑ How to make the contact angle (θ) small?

- By obtaining $(\gamma_{LM}-\gamma_{SM})$ closer to 1 -----> larger γ_{LM} and smaller γ_{SM}
- Choose an inoculant which can form a S-M interface with low γ_{SM}

Wetting ↑	cos 0°	1
	cos 90°	0
	cos 180°	-1

$$\Delta G^*_{het} = \frac{4\pi\gamma_{SL}^3}{3(\Delta G_v)^2}(2 - 3\cos\theta + cos^3\theta)$$



$$\cos\theta = \frac{(\gamma_{LM}-\gamma_{SM})}{\gamma_{SL}}$$

❑ How to achieve a lower γ_{SM}?

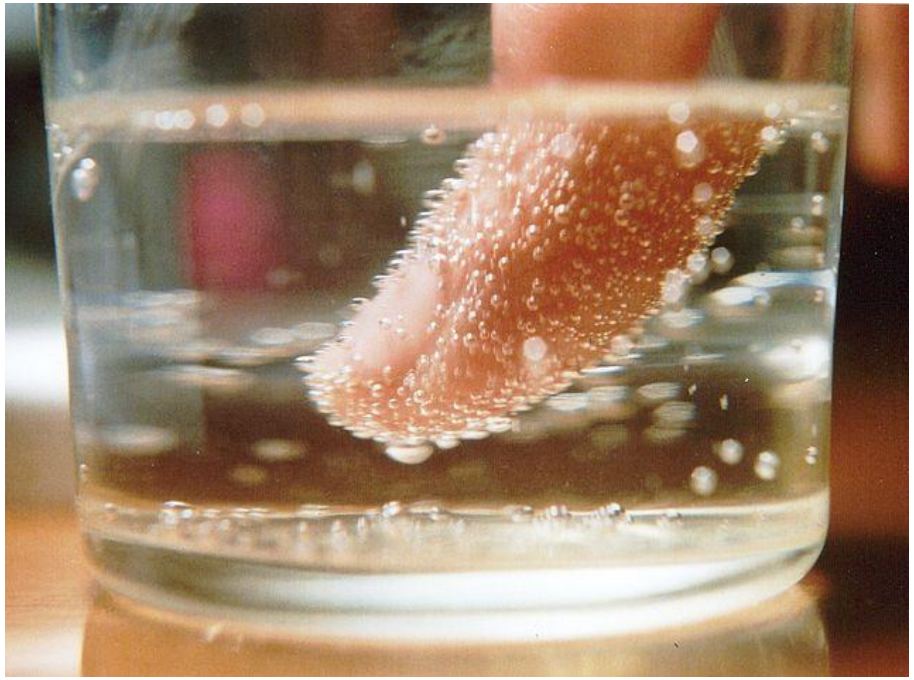
- Solid and inoculant have the same or a similar crystal structure
- Solid and inoculant have a similar lattice parameter, so as to have a fairly good matching at the interface.
- Nickel (FCC, 3.52 Å) as an inoculant in graphite (DC, 3.57 Å): helps producing artificial diamonds; TiB_2 to Al alloys

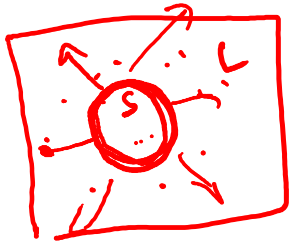
❑ Orientation relationship

- Orientation relationship (OR) between certain crystallographic planes and directions at the interface: OR between parent and product phases helps achieving a coherent interface, and promotes heterogeneous nucleation.

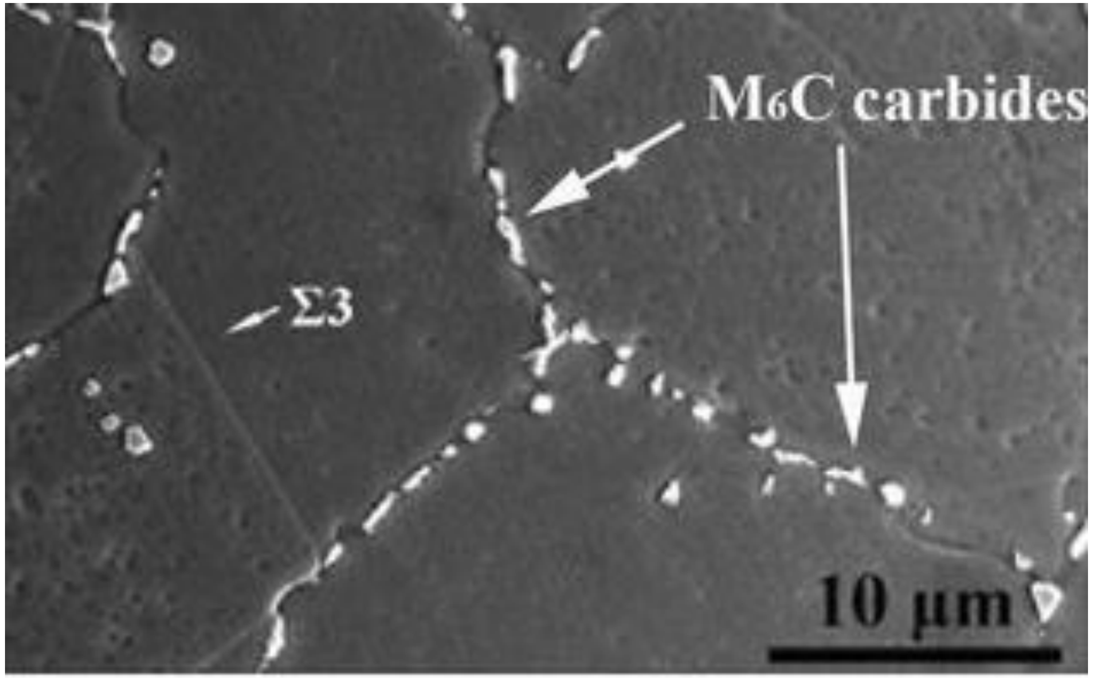
Heterogeneous nucleation

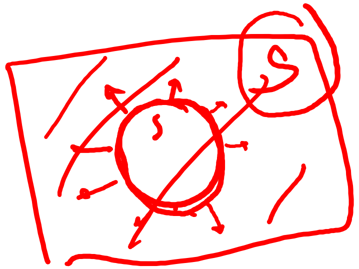
Nucleation in the liquid





Nucleation in the solid





stress (oppose transf.)

(change ΔG) $\propto$ ΔG_v, γ.

(solid surf.) $+ A \gamma_s$.

Why does we often encounter heterogeneous nucleation?

- The pre-exponential term is a function of the number of nucleation sites.
- The term that dominates is the exponential term and due to a lower ΔG^* the heterogeneous nucleation rate is typically higher.

$$I_{\text{homo}} \propto I^0_{\text{homo}}\, e^{-\left(\frac{\Delta G^*_{\text{homo}}}{kT}\right)}$$

= f(number of nucleation sites) ~ 10^{42}

$$I_{\text{hetero}} \propto I^0_{\text{hetero}}\, e^{-\left(\frac{\Delta G^*_{\text{hetero}}}{kT}\right)}$$

= f(number of nucleation sites) ~ 10^{26}

BUT
the exponential term dominates

$$\mathbf{I_{hetero} > I_{homo}}$$

MLL 100

Introduction to Materials Science and Engineering

Lecture-17 (February 12, 2022)

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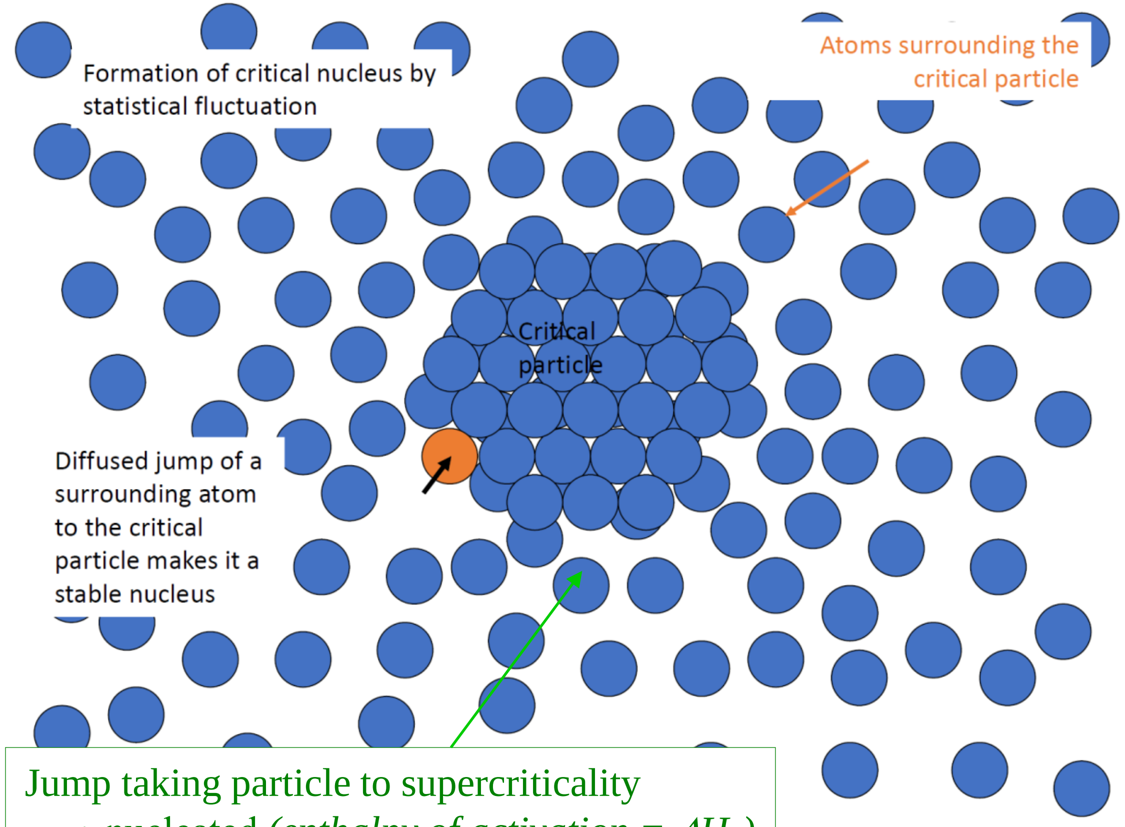
IIT Delhi
Department of Materials Science and Engineering

What have we learnt in Lecture-16?

- Heterogeneous nucleation
- Wetting property

Parameters influencing nucleation rate



Jump taking particle to supercriticality
→ nucleated *(enthalpy of activation = ΔH_d)*

- Potential atoms capable of jumping to make a critical nucleus supercritical are the atoms which are just 'adjacent' to the liquid, say s^*.

- If the ***lattice vibration frequency is*** ν and the ***activation barrier*** for an atom facing the nucleus (i.e. atom belonging to s*) to jump into the nucleus (to make in supercritical) is ΔH_d , the frequency with which nuclei become supercritical due atomic jumps into the nucleus

$$\nu' = s^* \nu \, e^{\left(-\frac{\Delta H_d}{kT}\right)}$$

Rate of nucleation = No. of critical sized particles × Frequency with which they become supercritical

$$I = \frac{dN}{dt}$$

$$N^* = N_t \, e^{\left(-\frac{\Delta G^*}{kT}\right)}$$

No. of particles/volume

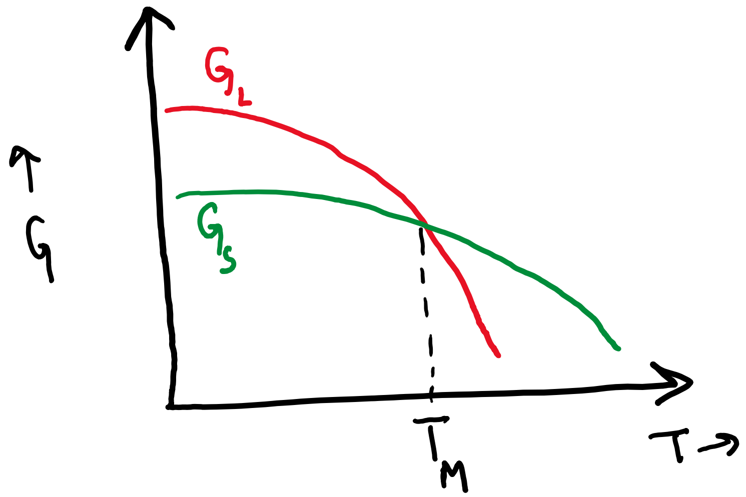
$$\nu' = s^* \nu \, e^{\left(-\frac{\Delta H_d}{kT}\right)}$$

ν → lattice vibration frequency (~10^{13} /s)

Dependence of Nucleation rate on Temperature

- How does the plot of nucleation rate vary with temperature?
  - At T_m , ΔG^* is $\infty \Rightarrow I = 0$ *(if there is no undercooling there is no nucleation).*
  - At T = 0 K again I = 0
- This implies that the function should reach a maximum between $T = T_m$ and T = 0.
- Nucleation rate is not a monotonic function of undercooling.

$$\Delta G^* = \frac{16\pi\gamma_{sl}^3}{3.(\Delta G_v)^2}$$

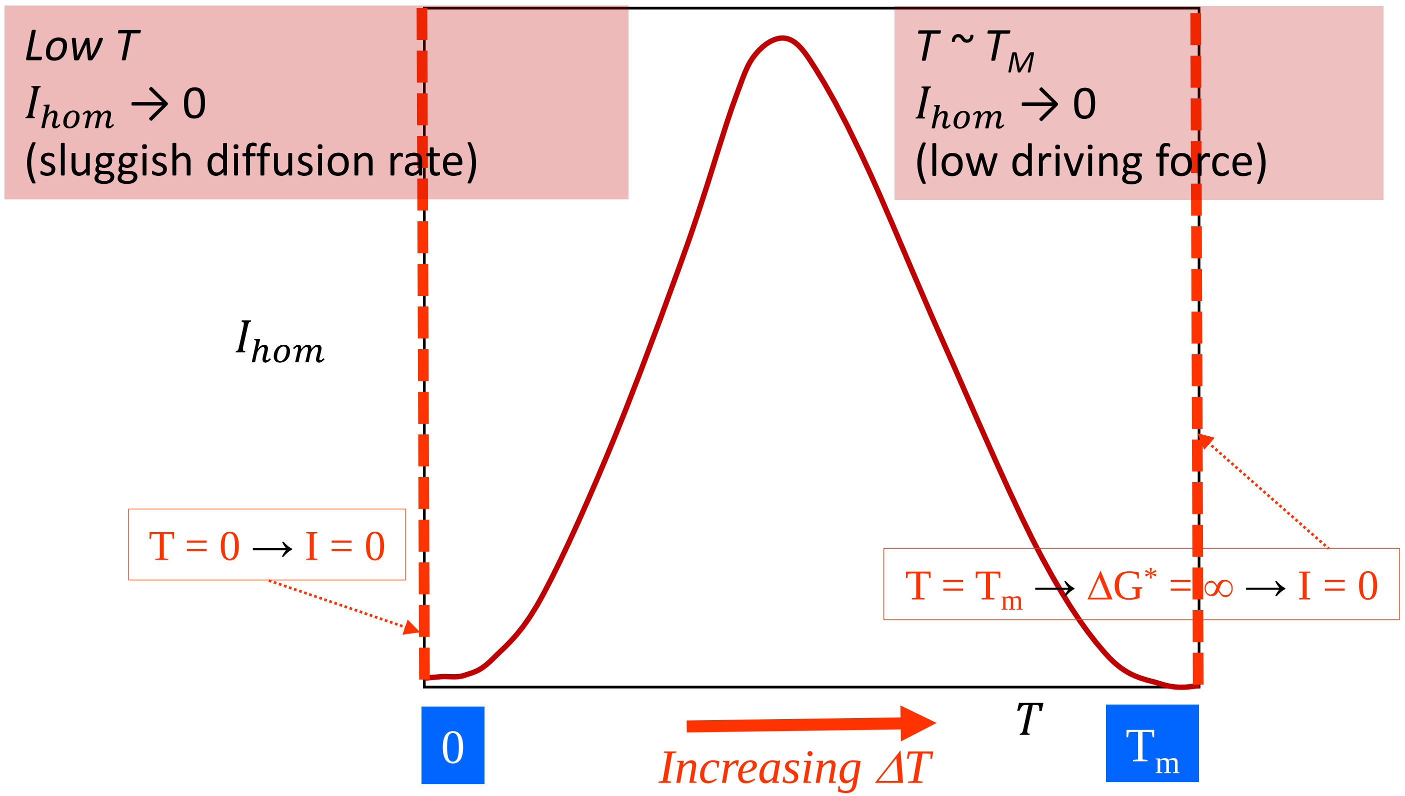


$$I = N_t\, s^*\, \nu\, e^{-\left(\frac{\Delta G^* + \Delta H_d}{kT}\right)}$$

- $\Delta G^* \uparrow \;\Rightarrow I \downarrow$

Note: ΔG^* is a function of T

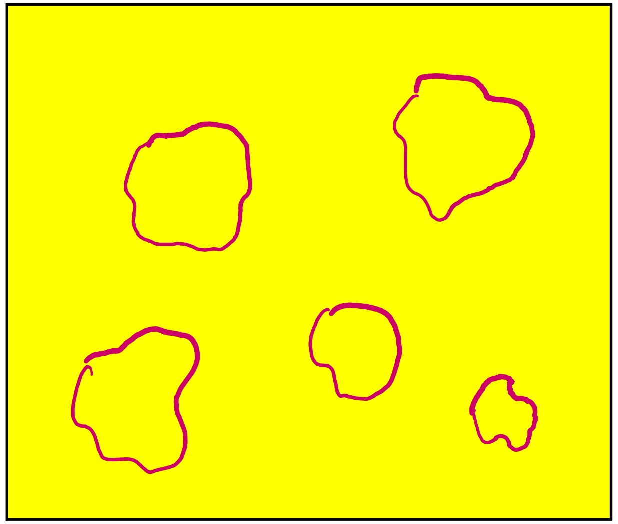
- $T \uparrow \;\Rightarrow I \uparrow$

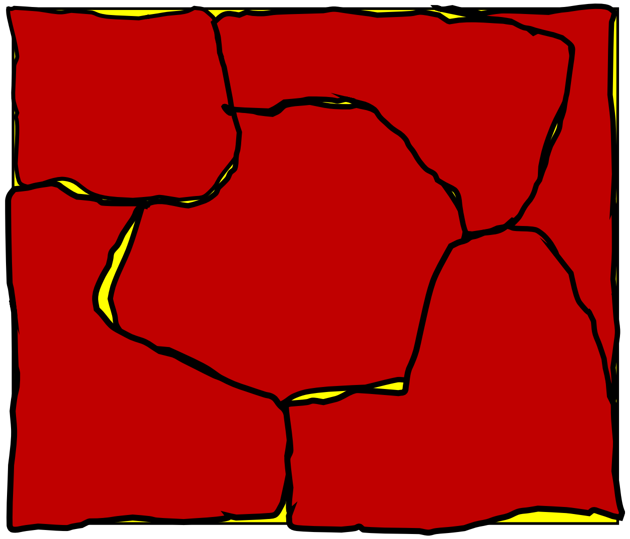


Growth rate

- Fraction of the product phase (solid phase) forming with time

  $\rightarrow$ the sigmoidal growth curve





- **Overall transformation rate,** $\boldsymbol{\frac{dX}{dt}}(\mathrm{s}^{-1})$: Fraction transformed (X) per second.
- **Nucleation Rate, I (in $\mathbf{m^{-3}s^{-1}}$):** No of nucleation events per unit volume per second.
- **Growth Rate,** $\boldsymbol{G=\frac{dR}{dt}}(\mathrm{ms}^{-1})$: Rate of increase of the size of growing particle.

$$\frac{dX}{dt} = f(I,G)$$

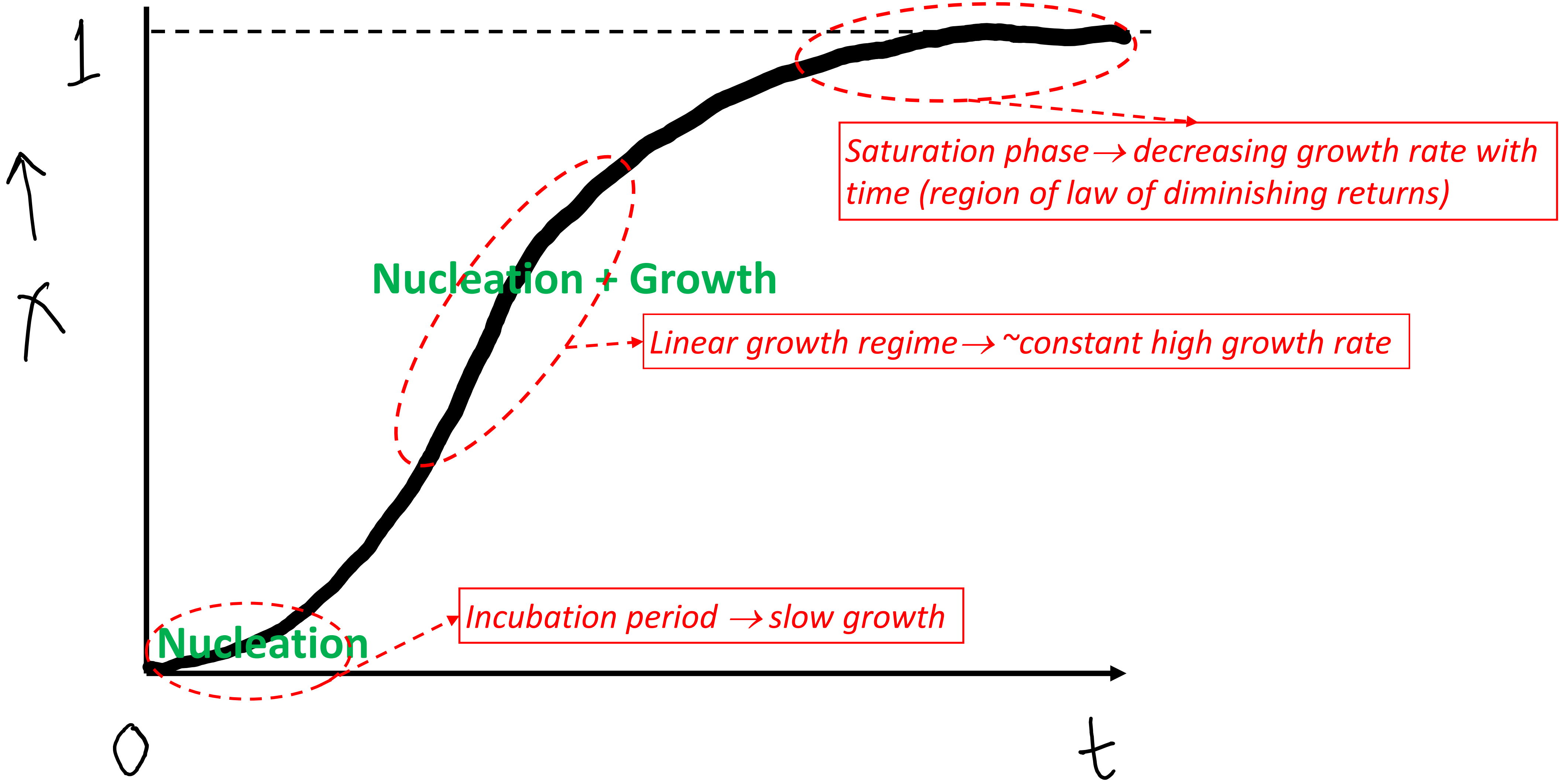
$$X = 1 - \exp\left(-\frac{\pi}{3} I G^3 t^4\right)$$

$$\frac{dX}{dt} = f(I, G)$$

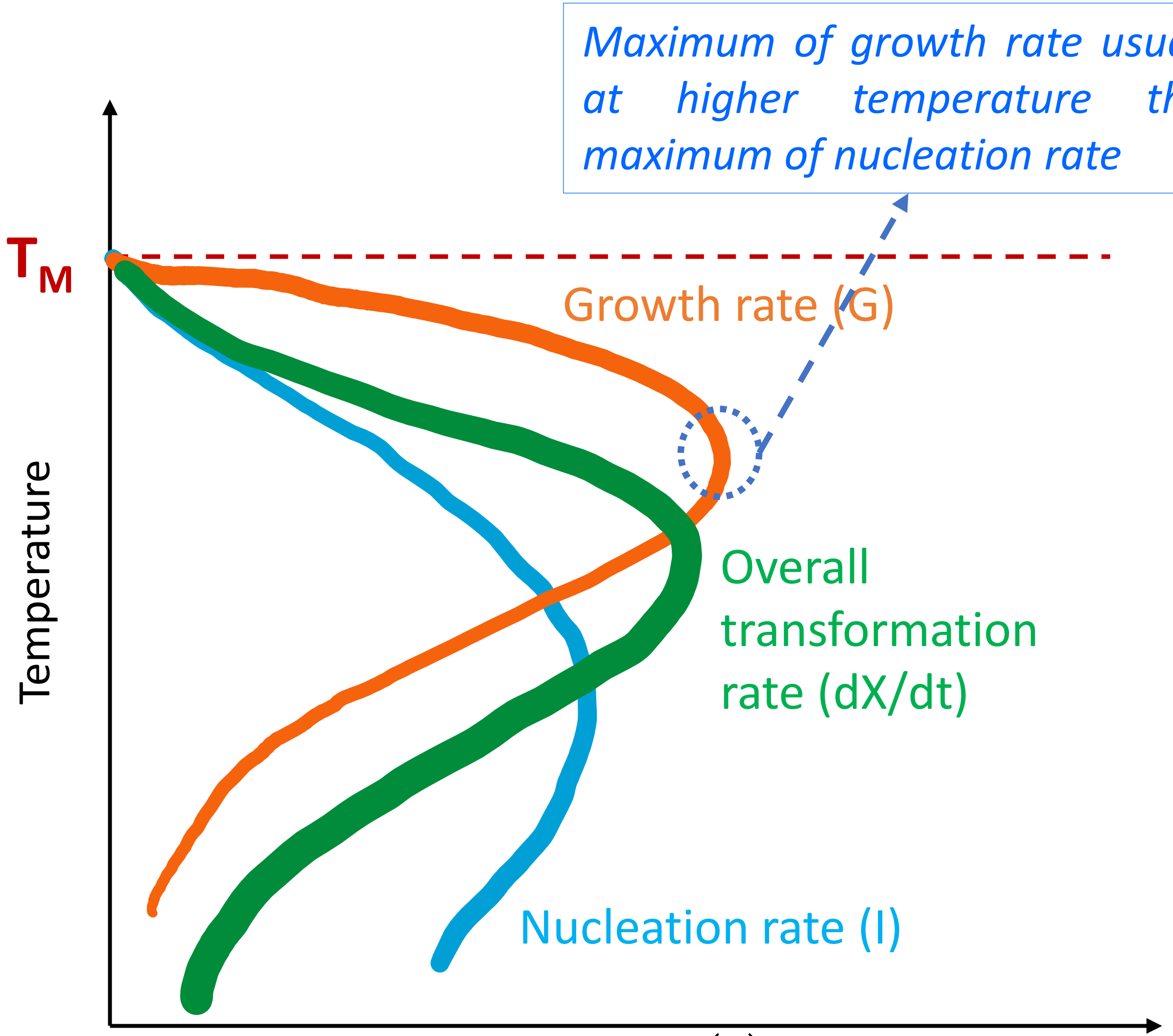
$$X = 1 - \exp(-\frac{\pi}{3} I G^3 t^4)$$

Nucleation slows down *because of reduction in driving force (less liquid)*

Growth slows down *because of grain impingement*

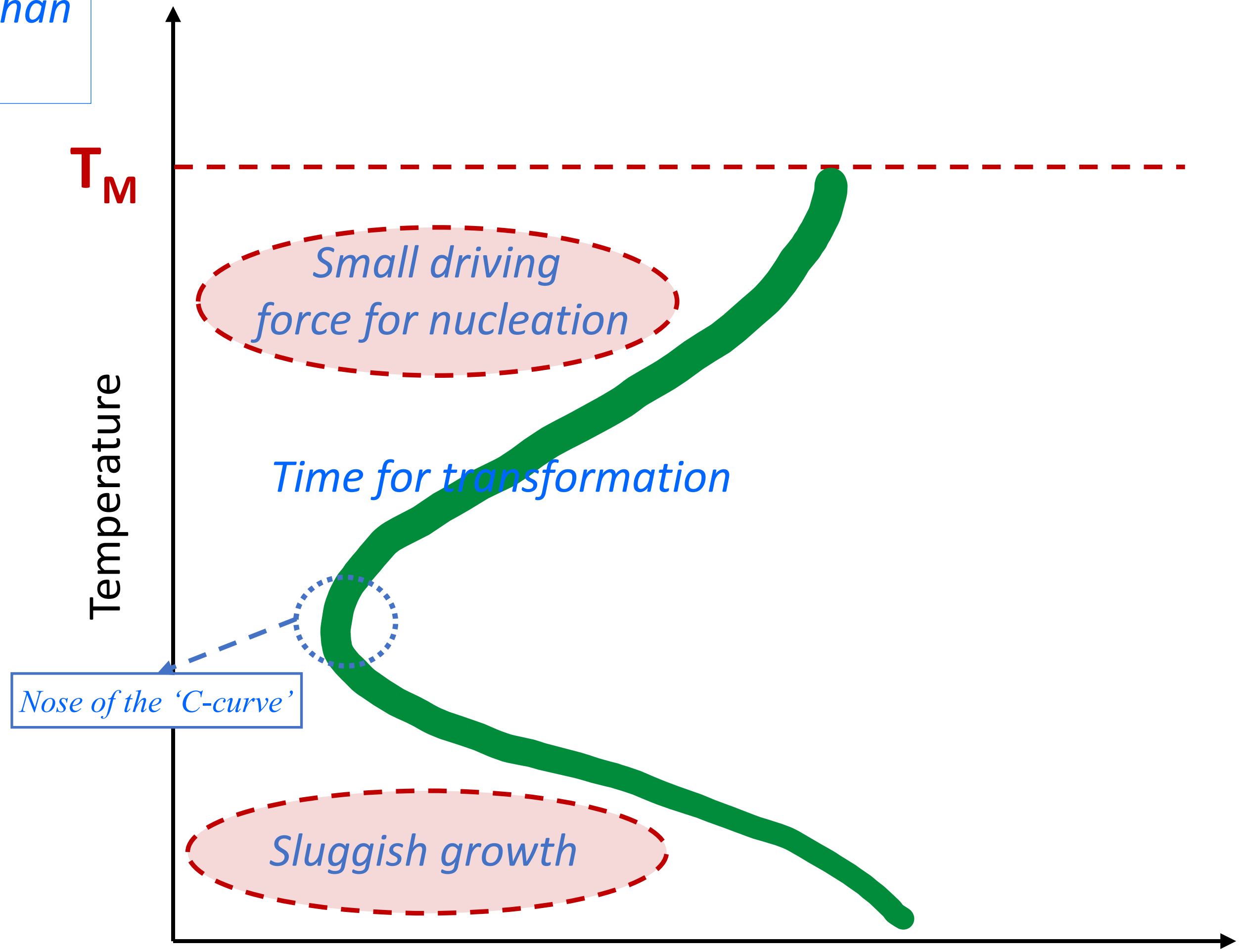


Transformation rate



Rate $\left(\frac{1}{t}\right)$

$$\frac{dx}{dt} \propto f(I, G)$$



Time ($t_{1/2}$)
(logarithmic scale)