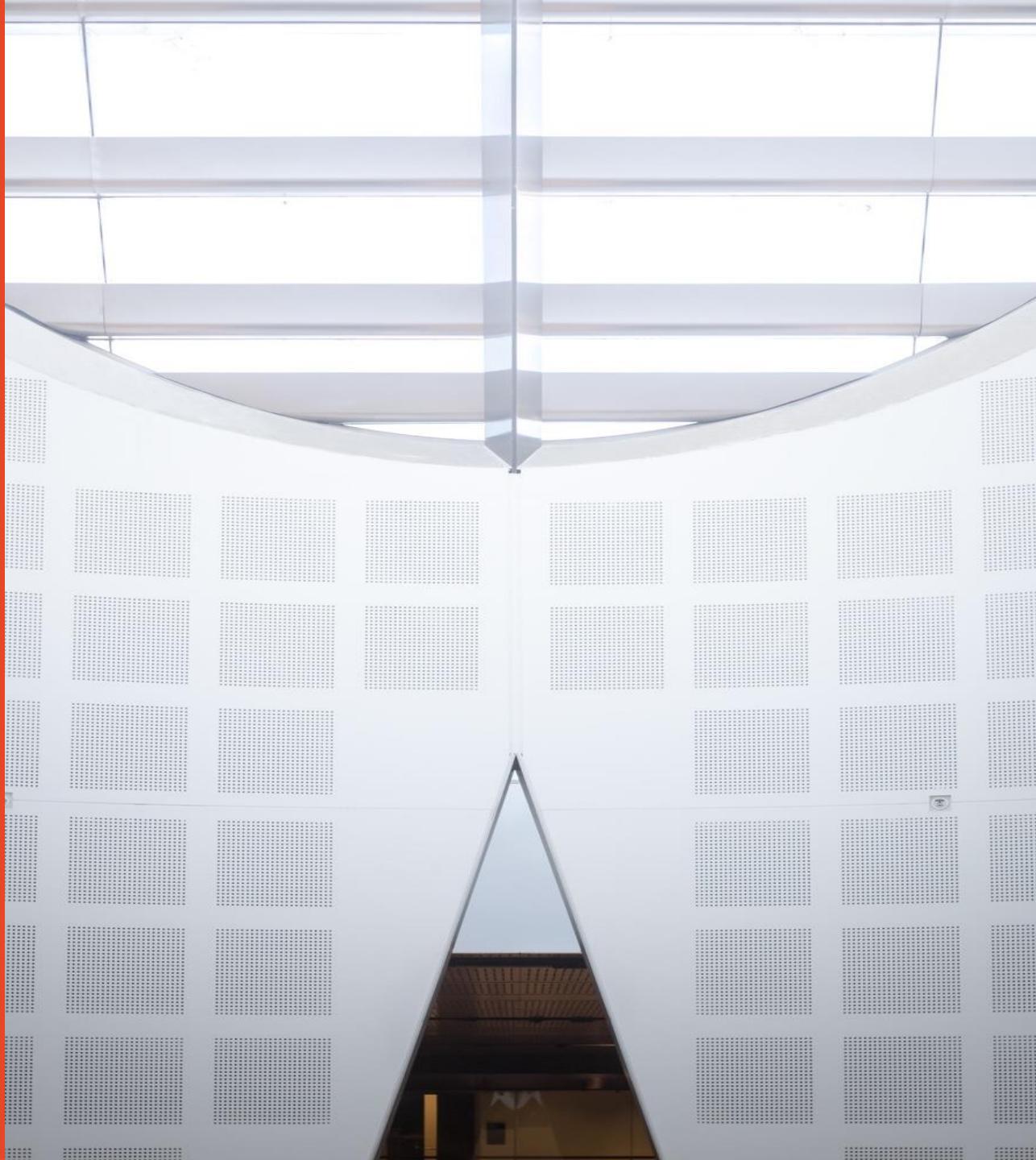


Solid State for Devices

Dr Marco Fronzi
School of Physics



THE UNIVERSITY OF
SYDNEY



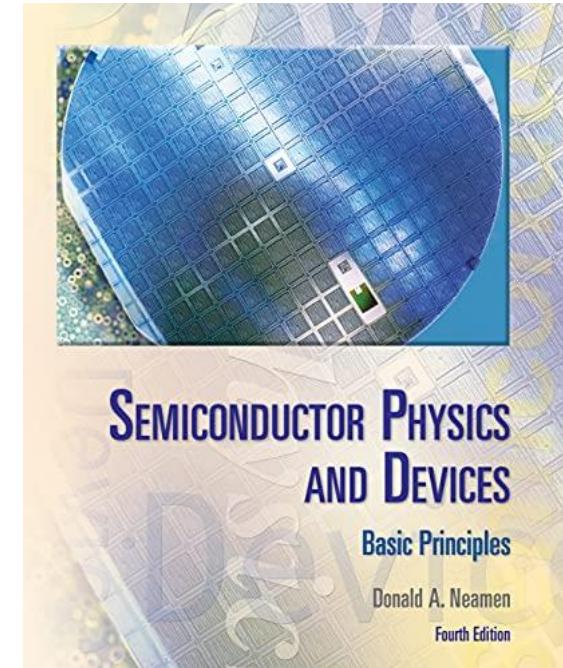
About Me

Marco Fronzi:

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Course Outline

- Textbook:
["Semiconductor Physics And Devices: Basic Principles" 4th Edition](#)
- Crystal Structures of Semiconductors
- Electronic Structures of Semiconductors
- Charge Carriers in Semiconductors
- Transport of Charge Carrier in Semiconductors
- Excess Charge Carriers in Semiconductors
- **Activities:**
 - 12 Lectures, Tuesdays 11am - 12pm (LT 2080, Belinda Hutchinson Building (H70), and 1pm - 2pm LT (Room 351), Education Building (A35)
 - Wednesdays 1-2pm, LT1 (Room 405), Physics Building (A28)
 - 4 Tutorials, Wednesdays 1-2 pm, Room 4001@Sydney Nano Hub & Online



Assessment Tasks

Assessment Task	Brief Description	Percentage Mark	Due Date	Learning Outcomes
PHYS 2213 SSD Assignment	Category: Submitted work Type: Assignment; Individual	2.5	Week 13/14	<u>1</u> , <u>2</u> , <u>4</u>
PHYS2213 SSD Quizzes (Four)	Category: In-class assessment Type: Small test; Individual Highest 3 out of 4 quizzes taken into account	1.5	Weekly (weeks 10-13)	<u>1</u> , <u>2</u> , <u>3</u> , <u>7</u>
Final examination: 2 hour online	Category: Exam Type: Final exam	20/60	Exam Period	<u>1</u> , <u>2</u> , <u>6</u> , <u>7</u>

Chapter 1

Crystal Structures of Semiconductors

Marco Fronzi

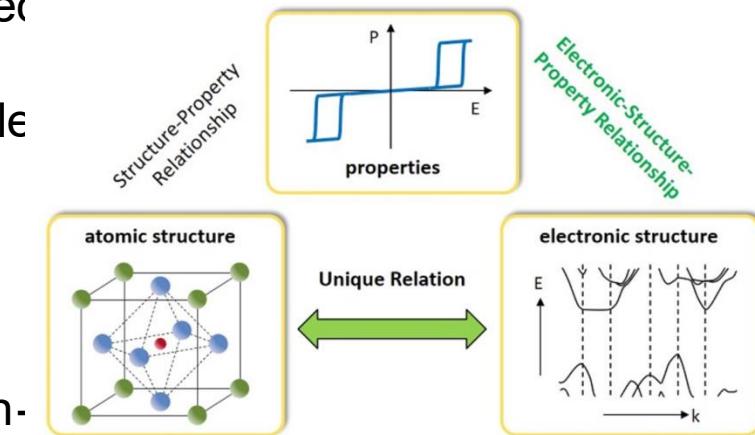
Marco.Fronzi@sydney.edu.au

What is Solid State Physics

Solid State Physics is the branch of physics that deals with the physical properties of matter in the solid phase.

It applies the principles of quantum mechanics, statistical mechanics, and electromagnetism to explain how the microscopic arrangement of atoms and electrons in a solid gives rise to macroscopic physical properties.

- **Electronic states and bands:** Formation of conduction and valence bands, effective carriers, and energy gaps.
- **Charge carriers:** Both negatively charged electrons and positively charged “hole” quasiparticles contributing to transport phenomena.
- **Statistical mechanics:** The occupation of electronic states follows Fermi–Dirac statistics, dictating carrier densities and transport.
- **Defects and impurities:** Vacancies, interstitials, and dopants modify local electronic structure, enabling control of conductivity (e.g., n-doping in semiconductors).
- **Transport theory:** Mobility, conductivity, and diffusion are derived from Boltzmann transport equations and scattering mechanisms.

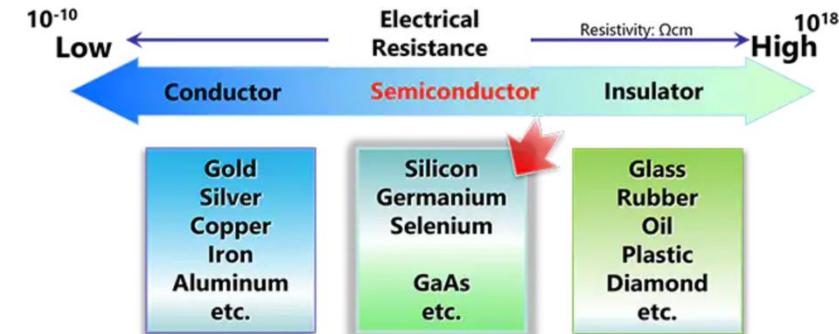


Classification of Solids Based on Electronic Properties

Classes of Materials (by Electrical Properties)

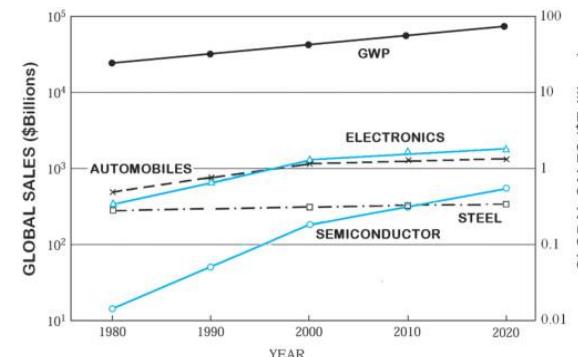
Conductors: Materials that allow electric current to flow easily.

- **Mechanism:** They possess a "sea" of loosely bound, mobile electrons in their outermost shells that can move freely when an electric field is applied.
- **Examples:** Metals like copper, aluminum, and silver.



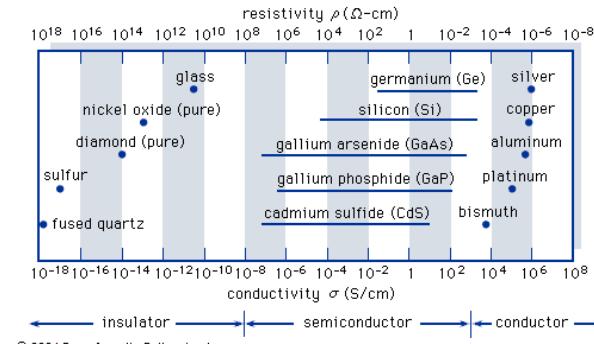
Insulators: Materials that resist the flow of electric current.

- **Mechanism:** They have tightly bound electrons that are not free to move and carry charge.
- **Examples:** Ceramics, wood, and plastics.



Semiconductors: Materials with electrical conductivity between that of conductors and insulators.

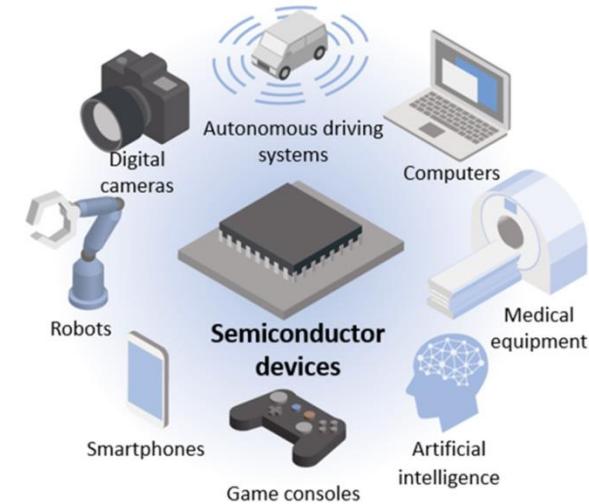
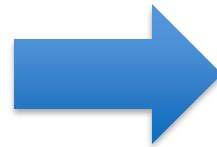
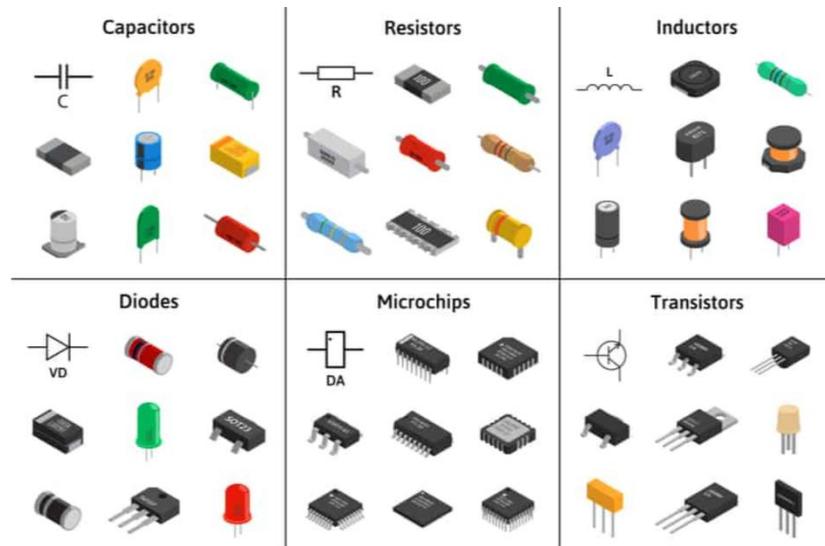
- **Mechanism:** Their conductivity can be significantly influenced by external factors. Temperature, exposure to electric fields or light, and the addition of impurity atoms
- **Examples:** Silicon and germanium



What are Semiconductors

Semiconductors are an essential component of electronic devices, enabling advances in communications, computing, healthcare, military systems, transportation, clean energy, and countless other applications.

- **Electronics** = charge carriers only (current, voltage, switching, amplification).
- **Optoelectronics** = charge carriers + photons (generation or detection of light).

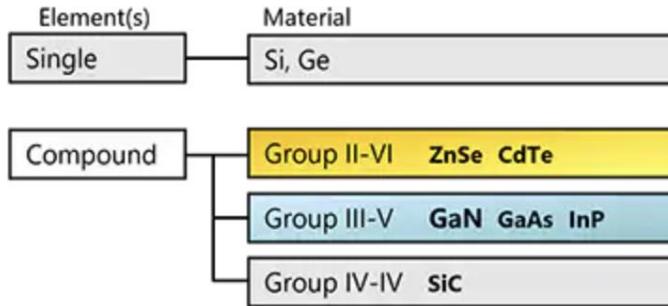


Key Idea: Metals → always conducting. Insulators → never conducting (under normal conditions). Semiconductors → conductivity can be tuned!

What are Semiconductors

*Doping phosphorus (P) of **Group V** into silicon (Si) of **Group IV** makes n-type semiconductor.

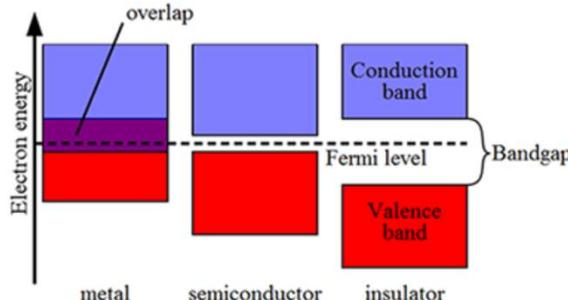
*Doping boron (B) of **Group III** into silicon (Si) of **Group IV** makes p-type semiconductor.



Group II	Group III	Group IV	Group V	Group VI
Be Beryllium	B Boron	C Carbon	N Nitrogen	O Oxygen
Mg Magnesium	Al Aluminum	Si Silicon	P Phosphorus	S Sulfur
Zn Zinc	Ga Gallium	Ge Germanium	As Arsenic	Se Selenium
Cd Cadmium	In Indium	Sn Tin	Sb Antimony	Te Tellurium
Hg Mercury	Tl Thallium	Pb Lead	Bi Bismuth	Po Polonium

Band Structure

Electrical properties of metals and semiconductors are determined by their electron and crystal structure. Simplified band structure shows the basic difference between metals, semiconductors and insulators.



Semiconductor	Group	Band gap (eV)
Elemental	Si	IV
	Ge	IV
Compound	CdS	II-VI
	CdSe	II-VI
	ZnSe	II-VI
	GaN	III-V
	GaAs	III-V
	GaP	III-V
	SiC	IV-IV

Elemental Semiconductors vs

	Elemental semiconductors	Compound semiconductors
1	These are made from single element. (mixed) element.	These are made from compound
2	These are made from IV group and VI group elements	These are made from III and V [or] II and VI elements
3	These are called as indirect band gap semiconductor (electron-hole recombination takes place through traps)	These are called as direct band gap semiconductor (electron-hole recombination takes place directly)
4	Heat is produced in the recombination	Photons are emitted during recombination
5	Life time of charge carriers is more due to indirect recombination	Life time of charge carriers is less due to direct recombination
6	Current amplification is more	Current amplification is less.
7	These are used for making diodes, transistor, etc.	These are used for making LED, laser diodes, etc.
8	Example : Ge, Si	Example : GaAs, GaP, CdS, MgO

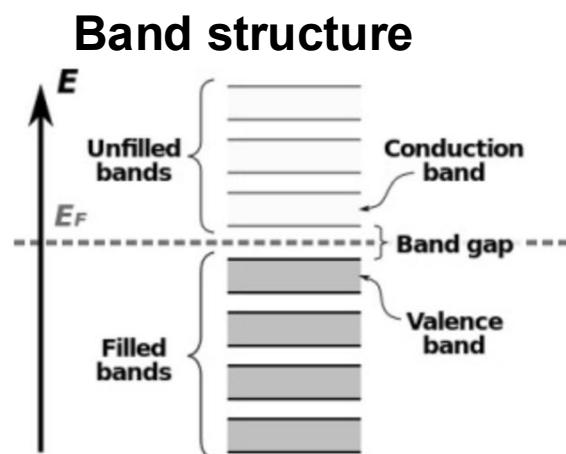
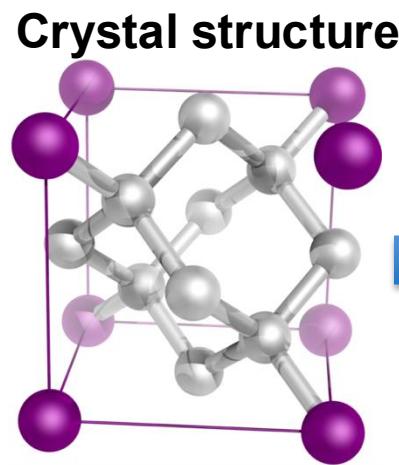
Band Theory

The **periodic arrangement of atoms in crystals** determines how atomic orbitals overlap and interact. This periodic potential gives rise to the formation of **allowed and forbidden energy bands**, as described by **band structure theory**.

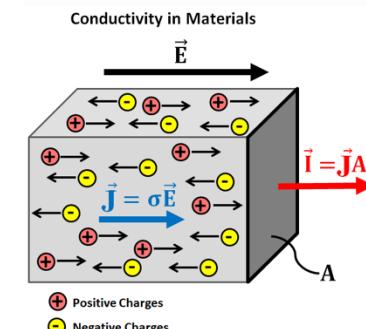
Band theory is the quantum-mechanical description of the energy levels of electrons in a crystalline solid.

Thus:

- **Crystal structure** → defines periodicity and bonding.
- **Band theory** → explains how this periodicity produces electronic states.
- **Electronic properties** → emerge as measurable conductivity, mobility, and optical response.

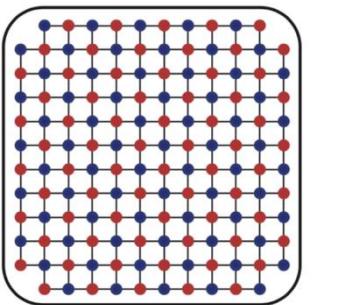


Electronic Properties

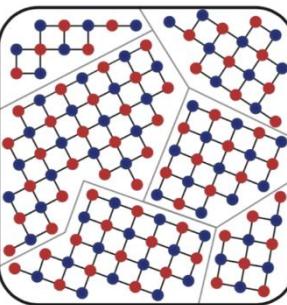


Types of Solid based on atomic arrangement

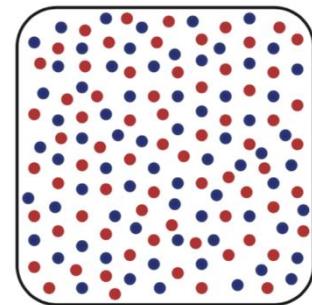
An ordered region is a spatial volume in which atoms or molecules have a regular geometric arrangement or periodicity. Amorphous materials have order only within a few atomic or molecular dimensions, while polycrystalline materials have a high degree of order over many atomic or molecular dimensions



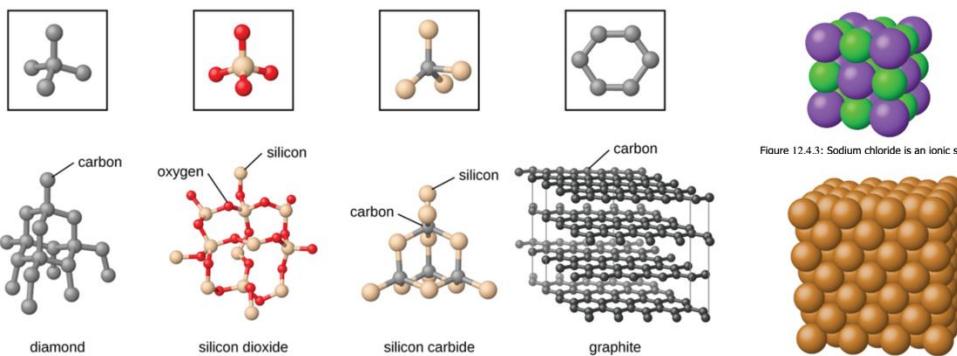
Crystalline



Polycrystalline



Amorphous

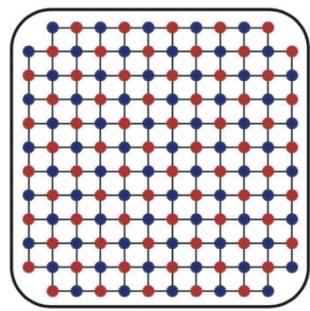
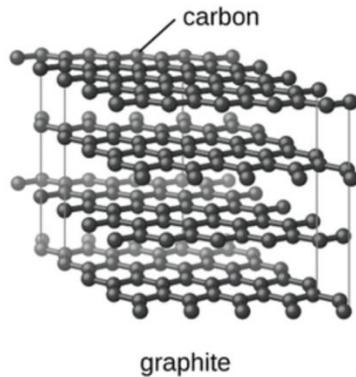


Importance of Crystal Quality

- Amorphous: cheap but low performance.
- Polycrystal: compromise between cost and efficiency.
- Single crystal: expensive, but necessary for high-performance devices.

Types of Solid based on atomic arrangement

In a single crystal, the atomic arrangement is perfectly periodic throughout the entire volume. This high degree of order ensures well-defined electronic band structures and superior electrical properties. Single crystals, like silicon wafers, are the foundation of modern semiconductor devices.



Crystalline

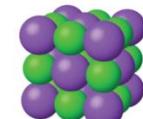


Figure 12.4.3: Sodium chloride is an ionic solid.

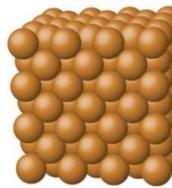
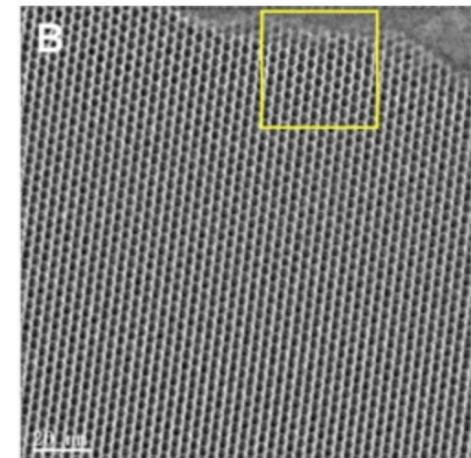
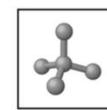
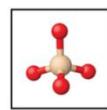


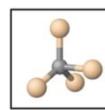
Figure 12.4.4: Copper is a metallic solid.



diamond



silicon dioxide

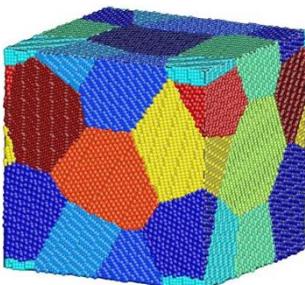
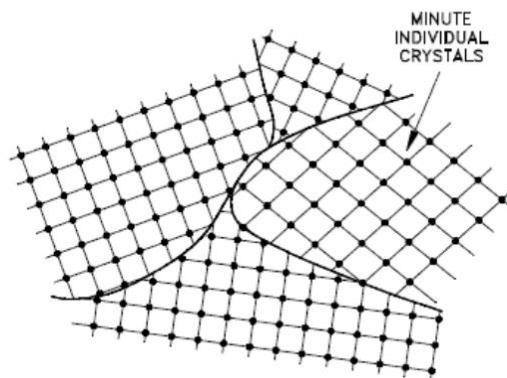
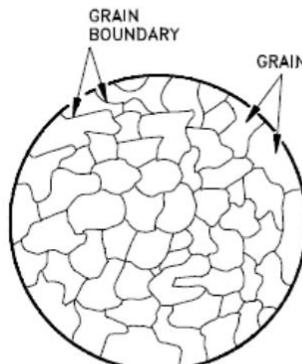
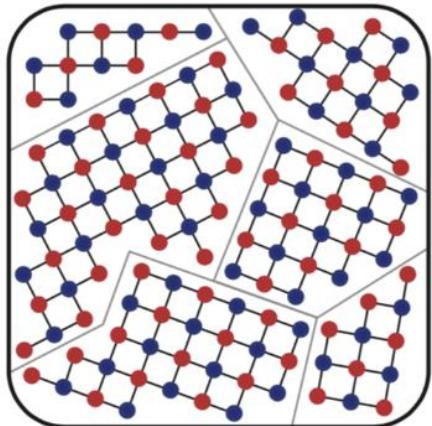


silicon carbide

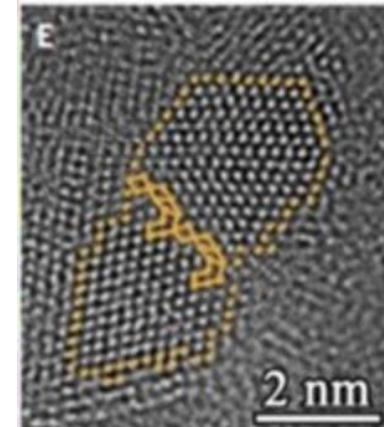
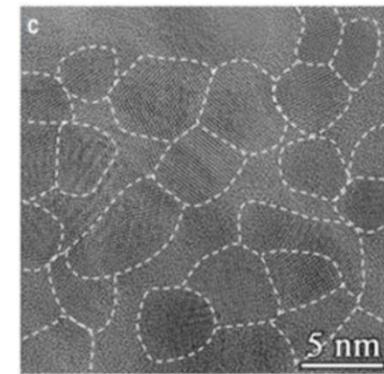
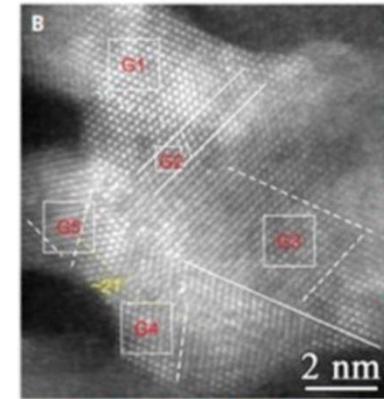
Polycrystals

- Composed of many small ordered regions (grains).
- Random grain orientations, separated by grain boundaries.
- Grain boundaries scatter carriers, reduce mobility.

Polycrystals are easier and cheaper to fabricate than single crystals and are used in solar cells and thin-film technologies.



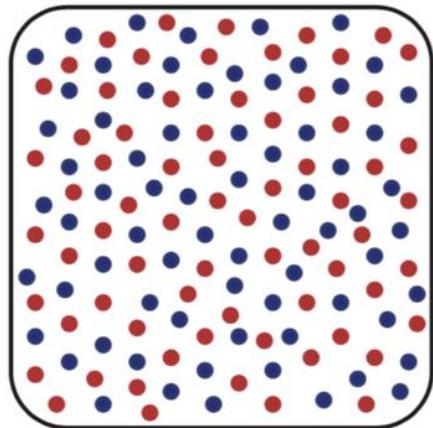
Polycrystalline



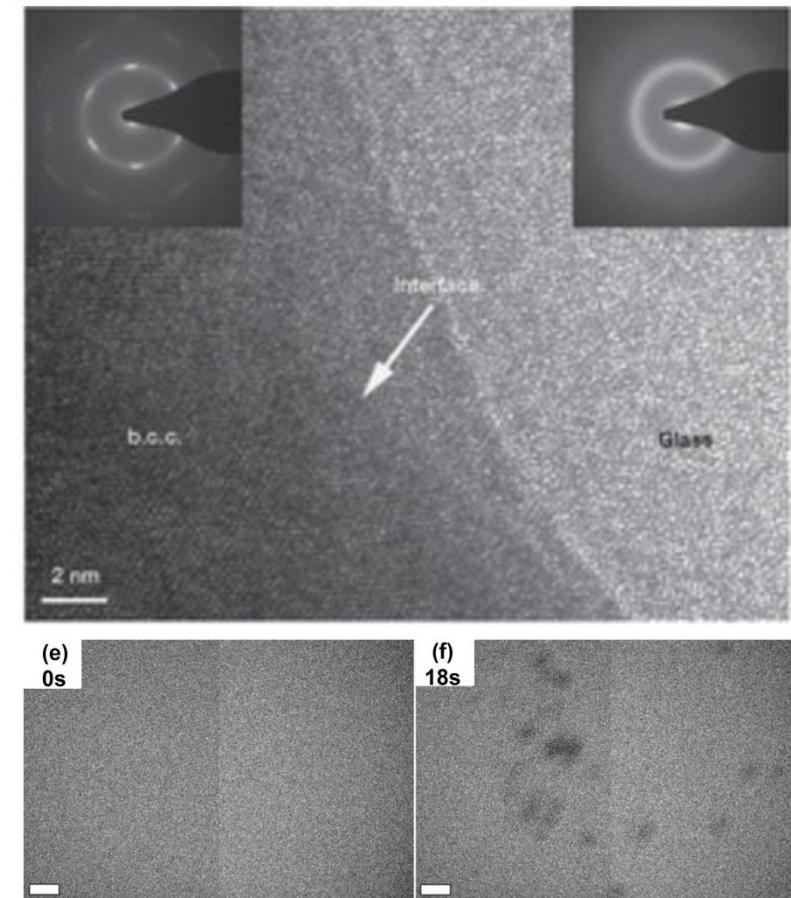
Amorphous Solids

Amorphous materials lack long-range periodic atomic order, with only short-range local arrangements. Their electronic states are localized, leading to lower mobility and poor conductivity compared to crystals. Amorphous semiconductors (e.g., a-Si:H) are widely used in thin-film transistors and photovoltaic applications.

- No long-range order, only short-range coordination.
- Example: glass, amorphous Si (used in thin-film solar cells).
- High density of defects → poor electrical performance.



Amorphous



Crystal Lattice Structure

A representative unit, or a group of atoms, is repeated at regular intervals in each of the three dimensions to form the single crystal. The periodic arrangement of atoms in the crystal is called the lattice.

A crystal unit cell is the smallest, **repeating unit** that, when copied and stacked, forms the entire crystal lattice. It's the basic building block of a crystal, and by repeating the unit cell in all directions, you can construct the entire crystal structure.

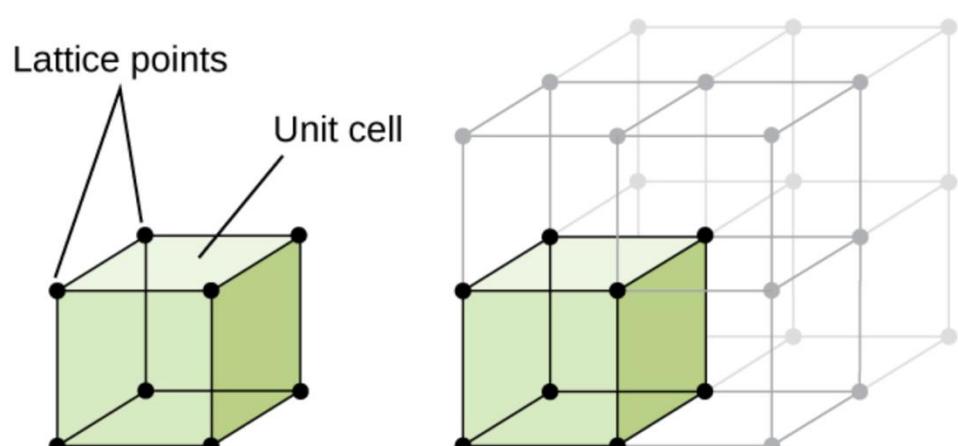


Figure 1. A unit cell shows the locations of lattice points repeating in all directions.

Characteristics of crystal lattice

Each constituent particle is represented by one point in a crystal lattice.

These points are known as lattice point or **lattice site**.

Lattice points in a crystal lattice are joined together by straight lines.

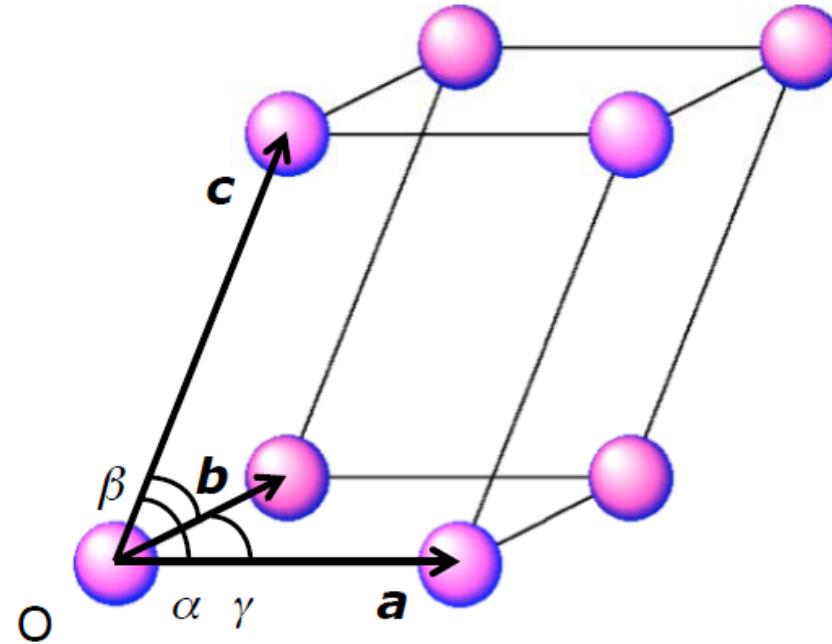
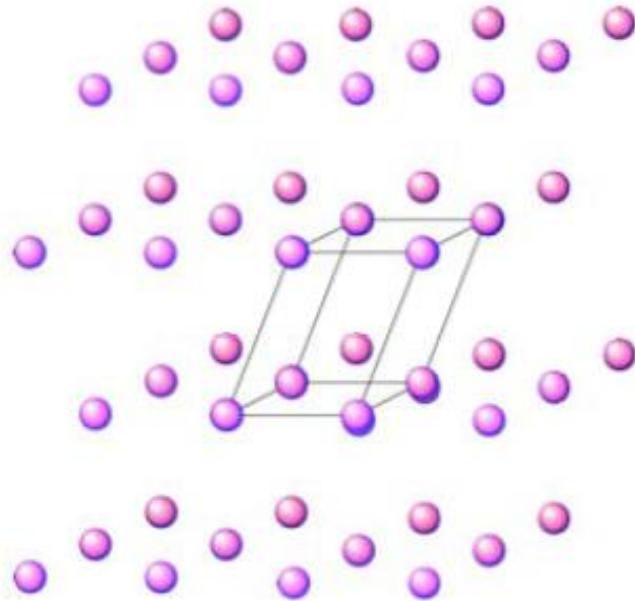
Parameters of a unit cell:

A unit cell is characterized by six parameters. These parameters are three edges (a , b and c) and angles between them . Dimensions along the edges of a unit cell is represented by a , b and c .

Edges of unit cell may or may not be mutually perpendicular.

The angle between b and c is represented by α , between a and c by β and between a and b by γ .

Unit Cell and Basis



a*, *b* and *c : crystal axes

$|a|$, $|b|$, $|c|$, α , β and γ : lattice constants

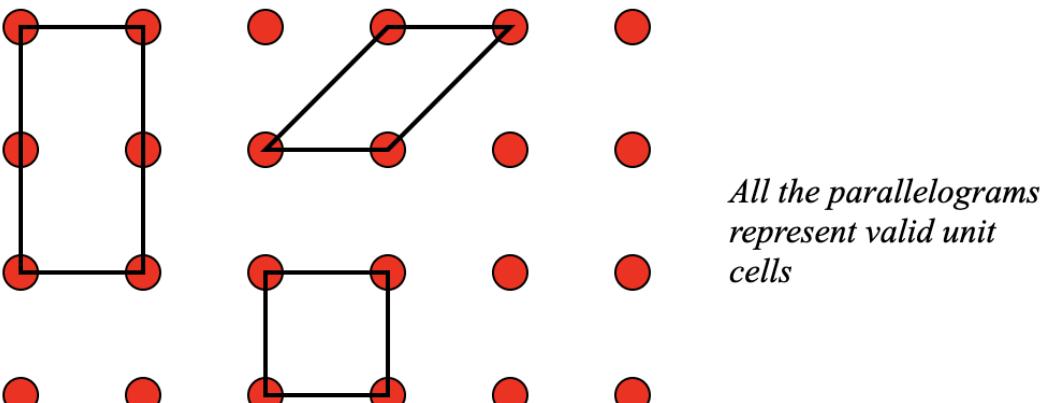
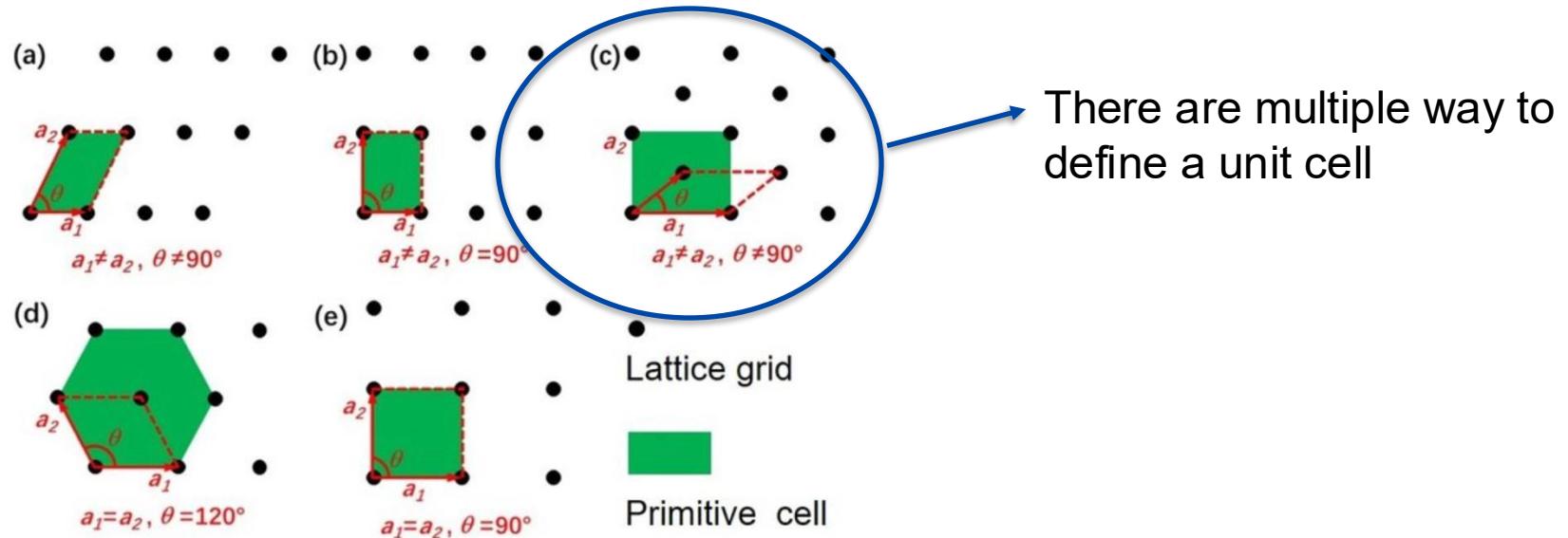
Positions of atoms : lattice points $R = ua + vb + wc$

2D Lattice Systems

In two dimensions, a lattice must fill all of space by periodic repetition of a unit cell without gaps or overlaps.

2D lattices fall into only
4 crystal systems:

1. Oblique
2. Rectangular
3. Hexagonal
4. Square



3D Lattice Systems

In three dimensions, a lattice must fill all of space by periodic repetition of a unit cell without gaps or overlaps.

- α = angle in the yz plane
- β = angle in the xz plane
- γ = angle in the xy plane

3D lattices fall into only
7 crystal systems:

- 1.Cubic
- 2.Tetragonal
- 3.Orthonhombic
- 4.Hexagonal
- 5.Rhombohedral (Trigonal)
- 6.Monoclinic
- 7.Triclinic

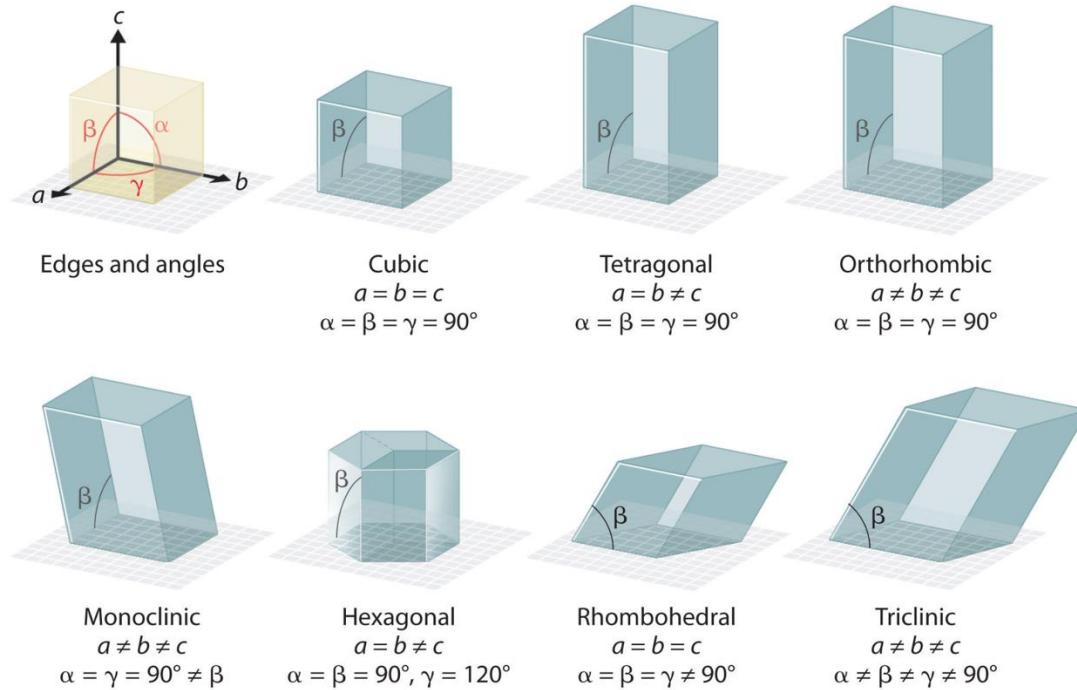


Figure 12.1.1: The 7 types of unit cells. In this class we will only look at cubic systems, and will identify 3 types of cubic unit cells (figure. 12.b)

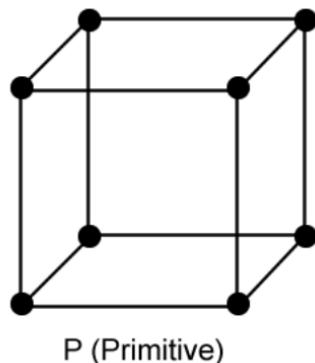
Crystal Lattice Structure

Primitive Unit Cells

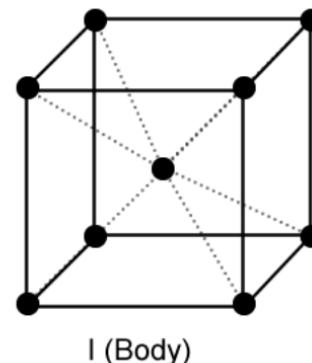
If the constituent particles of a crystal lattice are present only on the corner positions of a unit cell, it is known as primitive unit cell (contains only one point).

Centered Unit Cells

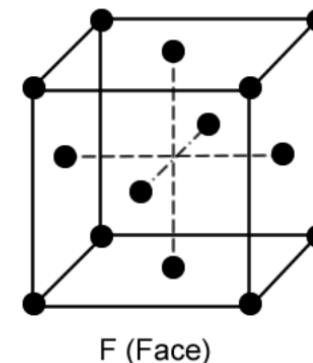
- If the constituent particles of a crystal lattice are present at positions other than corners in addition to those at corners, it is known as centered unit cell.
- Centered unit cells are of three types



P (Primitive)



I (Body)



F (Face)

Image 3: Types of Unit Cells

Crystal Unit Cells

Conventional Unit Cell

A unit cell selected for its convenient shape and ability to reveal the full symmetry of the crystal lattice.

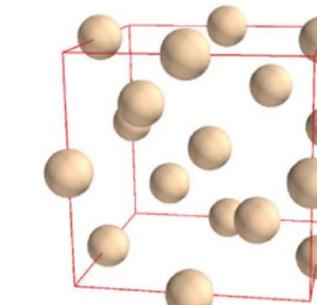
Lattice Points: May contain more than one lattice point.

Symmetry: **Chosen to show the overall symmetry of the crystal structure.**

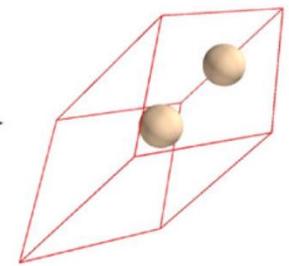
Purpose: To provide a clear and simple representation of the crystal's structure, even if it's not the smallest possible volume.

$$\bar{r} = p\bar{a} + q\bar{b} + s\bar{c}$$

Conventional unit cell



Primitive cell



Bravais Lattices

- A Bravais lattice is generated by the repetition of a unit cell (primitive or conventional) through all lattice translation vectors.

- It is uniquely generated by the repetition of primitive unit cells.
- It can also be represented by the repetition of conventional unit cells, which are not minimal but emphasise symmetry.

Symbols **P C I F R** refer to the different lattice types:

P = primitive, there is only 1 reticular point inside the cell.

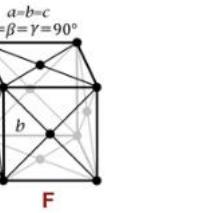
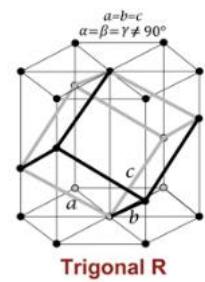
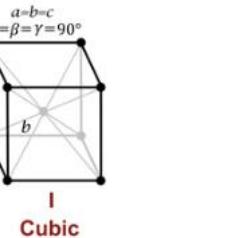
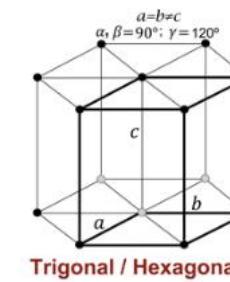
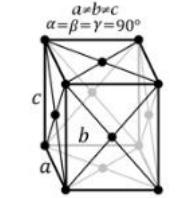
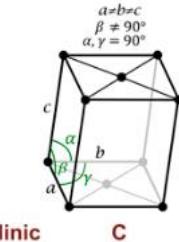
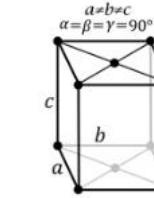
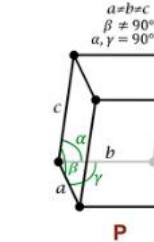
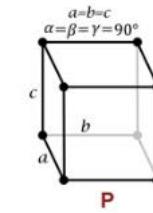
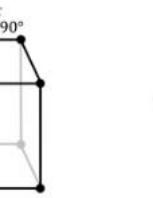
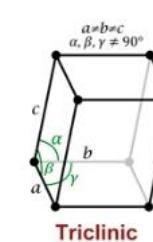
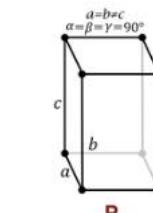
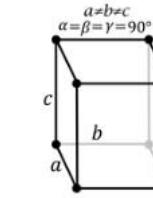
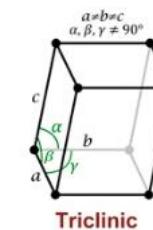
C = centered on the two faces perpendicular to the c axis of the unit cell.

I = centered in the body of the cell.

F = centered in all faces of the cell.

R = primitive, identical cell axes and cell angles, or hexagonal

$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3,$$

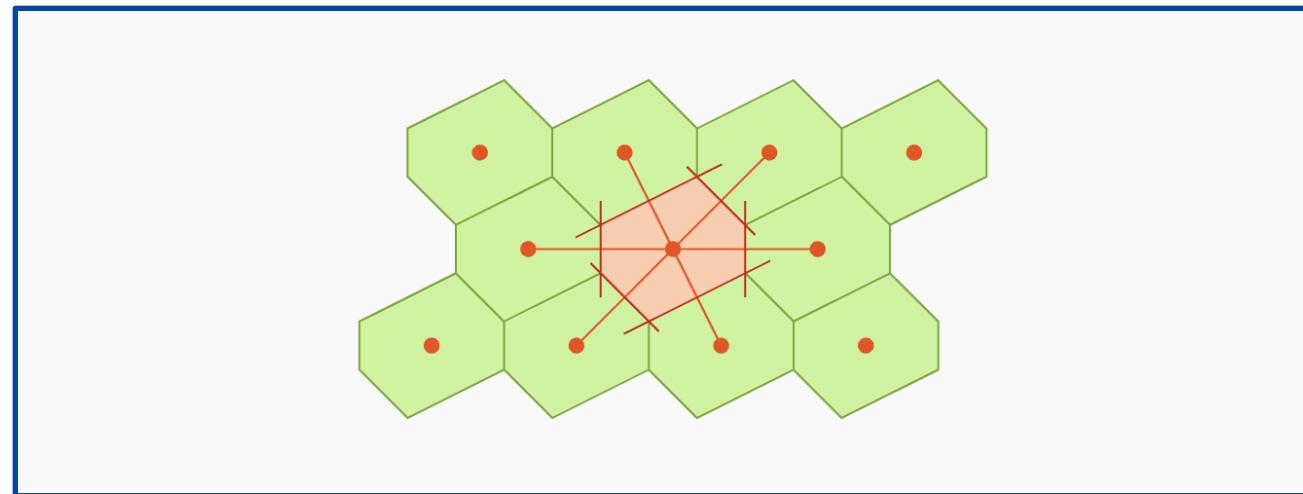


Wigner-Seitz cell

The Wigner-Seitz cell = a special type of primitive-cells

is a type of primitive cell in solid-state physics, constructing a unique, non-parallelepiped volume around a single lattice point by encompassing all points in space that are closer to that lattice point than to any other.

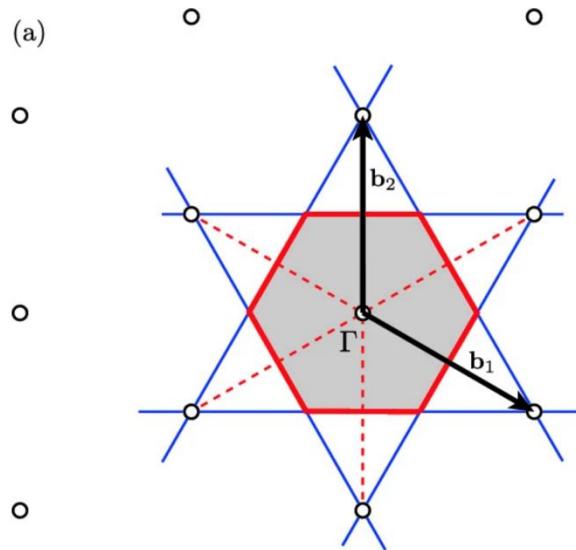
It is built by drawing lines to nearest neighbours and constructing their perpendicular bisectors to define the cell's boundaries, which depends on the specific Bravais lattice.



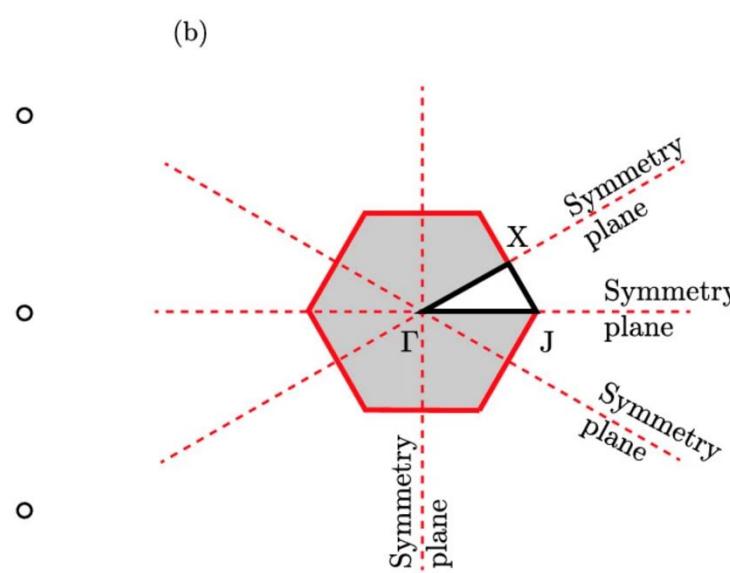
Brillion zone

To build the first Brillouin zone,
you plot the reciprocal lattice, designate a reciprocal lattice point as the origin,
draw lines to all its nearest neighbours,
and then construct perpendicular planes at the midpoints of these lines.

The smallest volume enclosed by these perpendicular planes is the **first Brillouin zone**.
Subsequent Brillouin zones are formed by continuing this process with the next-nearest neighbors and identifying the next smallest volume



(a)



(b)

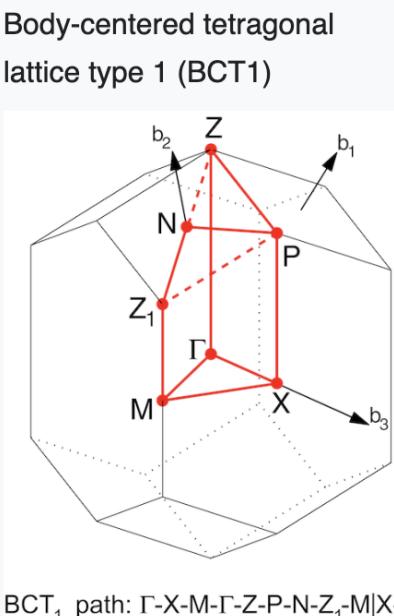
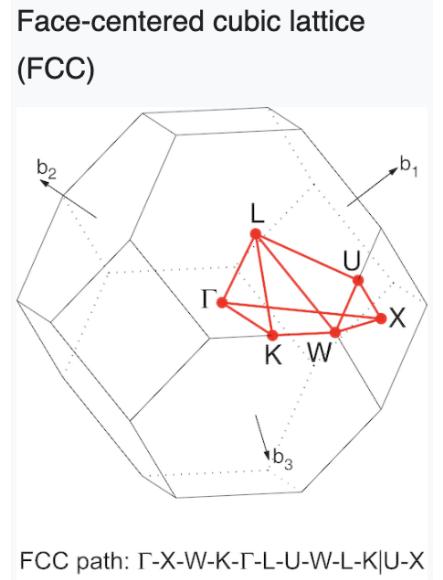
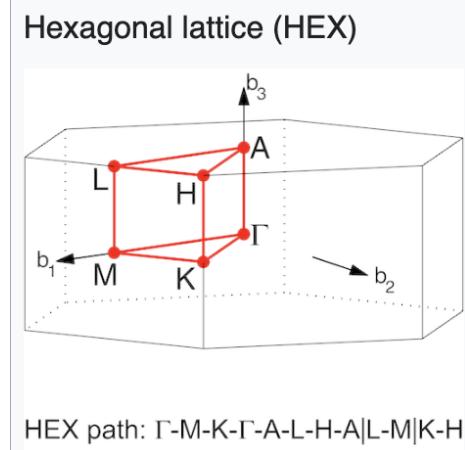
Reciprocal Lattice

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

a The reciprocal lattice of the hexagonal Bravais lattice and the first Brillouin zone (grey square), b the first Brillouin zone and the irreducible Brillouin zone ($\Gamma J X$) with $\Gamma : \frac{2\pi}{a} (0, 0)$, $J : \frac{2\pi}{a} (\frac{2}{3}, 0)$ and $X : \frac{2\pi}{a} (\frac{1}{2}, \frac{1}{2\sqrt{3}})$. Points Γ , J , and X are the points of highest symmetry in the irreducible Brillouin zone

High Symmetry points in Brillouin zone

Symbol	Description
Γ	Center of the Brillouin zone
Simple cube	
M	Center of an edge
R	Corner point
X	Center of a face
Face-centered cubic	
K	Middle of an edge joining two hexagonal faces
L	Center of a hexagonal face
U	Middle of an edge joining a hexagonal and a square face
W	Corner point
X	Center of a square face
Body-centered cubic	
H	Corner point joining four edges
N	Center of a face
P	Corner point joining three edges
Hexagonal	
A	Center of a hexagonal face
H	Corner point
K	Middle of an edge joining two rectangular faces
L	Middle of an edge joining a hexagonal and a rectangular face
M	Center of a rectangular face



Symmetries

But lattices only tell us how points repeat in space. they do not yet capture the full symmetry of a crystal Transformation that leaves an object or structure unchanged in its overall appearance or properties In addition to simple translation, crystals may also possess **rotational, reflection, inversion, or combined symmetries.**

Group Theory is a mathematical framework for symmetries

Crystallography applies group theory to periodic atomic arrangements.

Types of Symmetry Operation

Translation: This is a periodic repetition of the crystal lattice in space.

Identity: The operation of doing nothing, which always leaves an object unchanged.

Rotation: Rotation around an axis leaves the crystal looking identical after rotating by a specific angle (e.g., 180° , 90° , 60°). The possible axes in a crystal are 1-, 2-, 3-, 4-, and 6-fold rotation axes.

Reflection: A mirror plane divides the crystal into two identical halves, where one half is the perfect mirror image of the other.

Inversion: An inversion operation involves passing through a center of symmetry, where every point in the crystal has an equivalent point directly opposite it through this center.

Improper Rotation (Roto inversion): An operation that combines a rotation with an inversion through a center of symmetry.

1. Identity, E
2. Rotation, C_n
3. Reflection, σ
4. Inversion, i
5. Improper Rotation, S_n

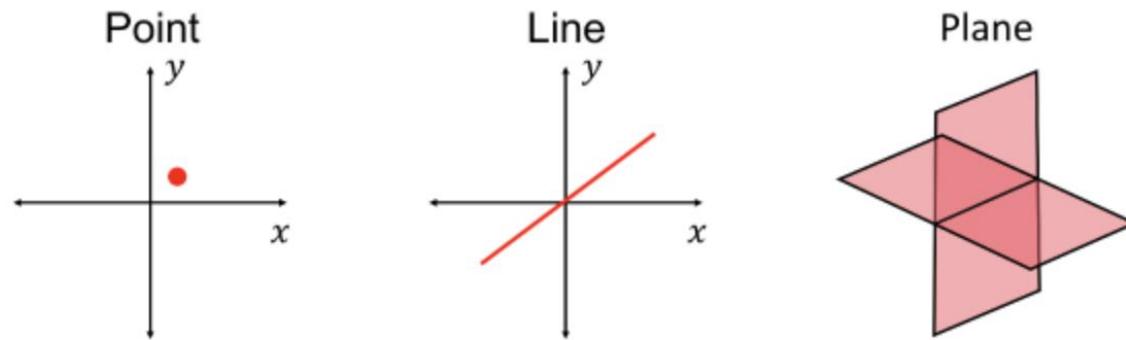
Glide Planes: Reflection + translation parallel to the mirror plane.

Screw Axis: A combination of a proper rotation and a translation along the axis of rotation.

Symmetries

Transformation that leaves an object or structure unchanged in its overall appearance or properties

Symmetry Elements



1. Identity, E
2. Rotation, C_n
3. Reflection, σ
4. Inversion, i
5. Improper Rotation, S_n

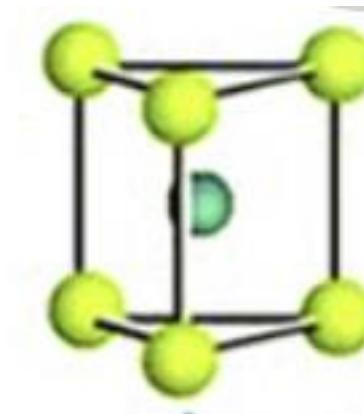
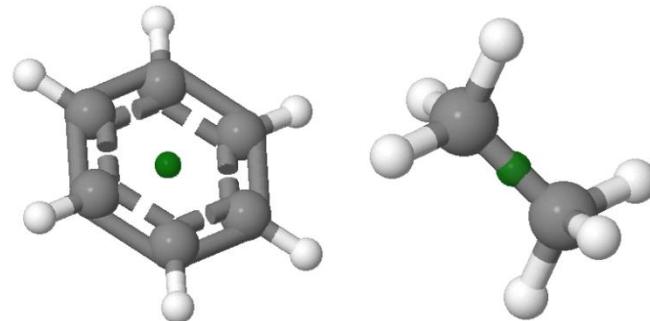
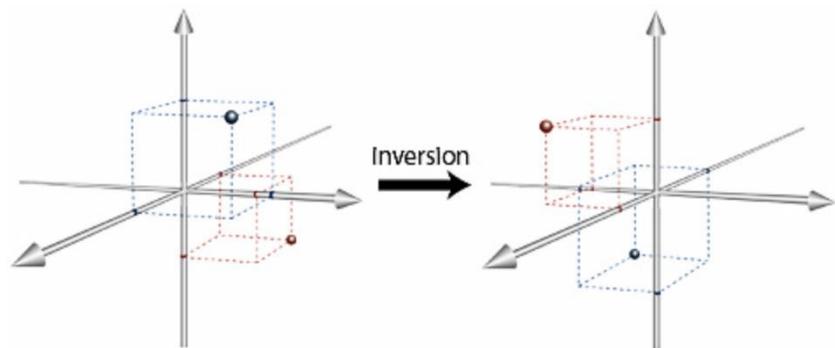
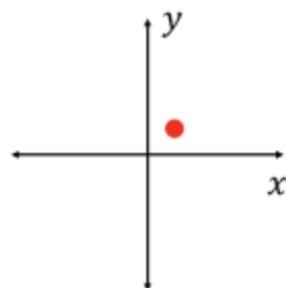
Symmetries

Transformation that leaves an object or structure unchanged in its overall appearance or properties

Inversion:

Symmetry Elements

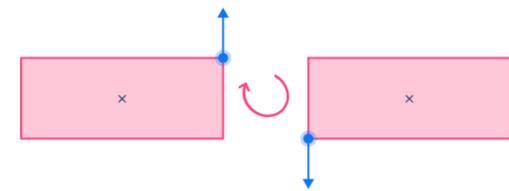
Point



Symmetries

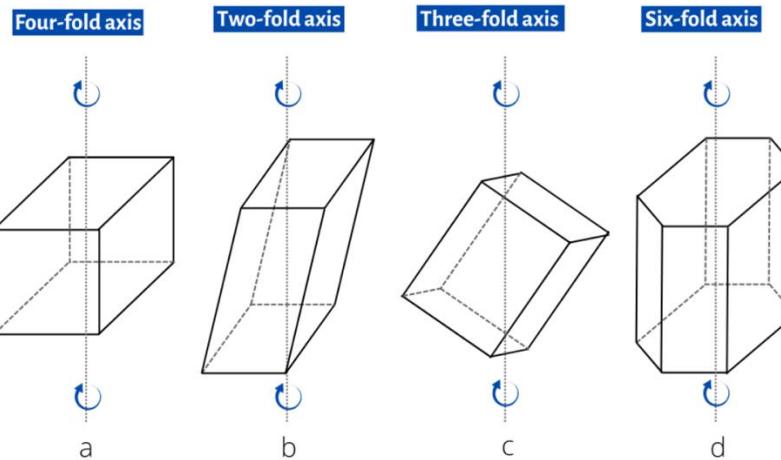
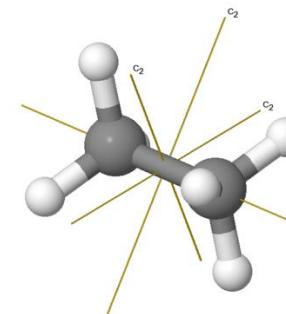
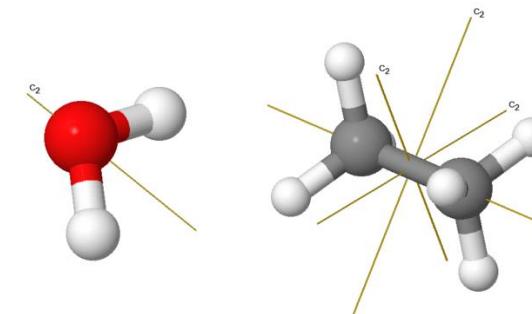
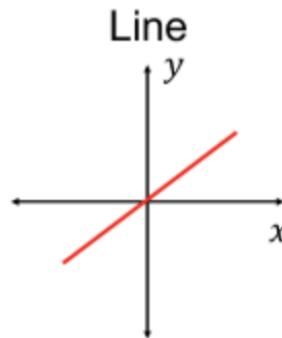
Transformation that leaves an object or structure unchanged in its overall appearance or properties

Rotation:



2D Polygon	Equilateral Triangle	Square	Regular Pentagon	Regular Hexagon
Order of Rotational Symmetry	3	4	5	6

Symmetry Elements

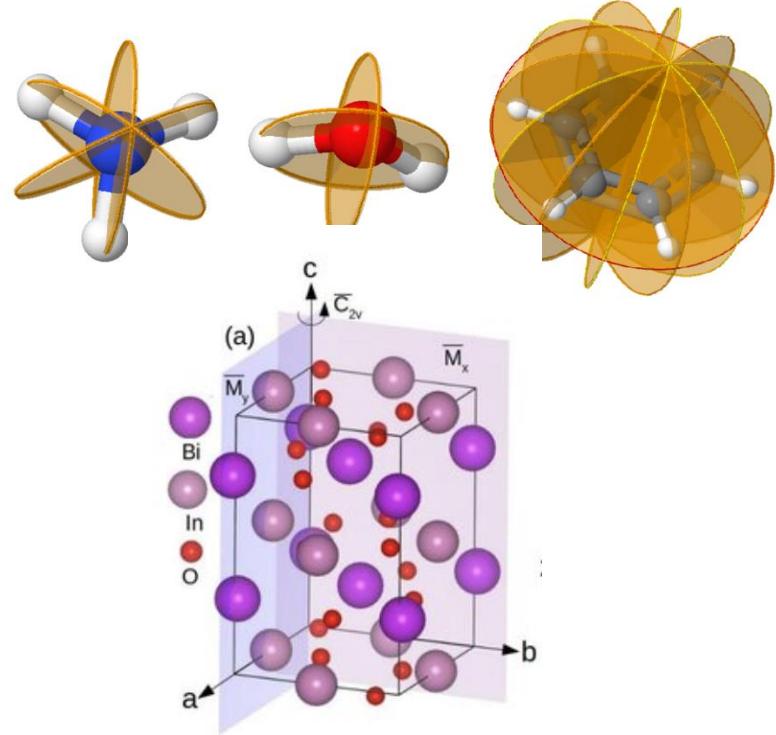
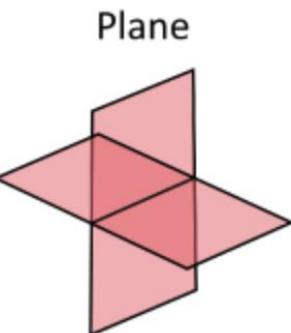
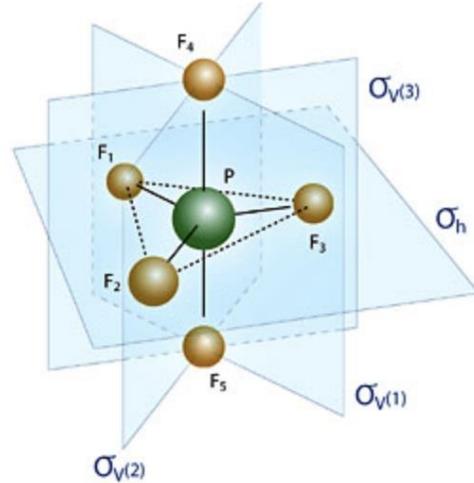


Symmetries

Transformation that leaves an object or structure unchanged in its overall appearance or properties

Reflection:

Symmetry Elements

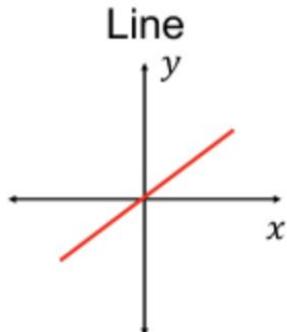


Symmetries

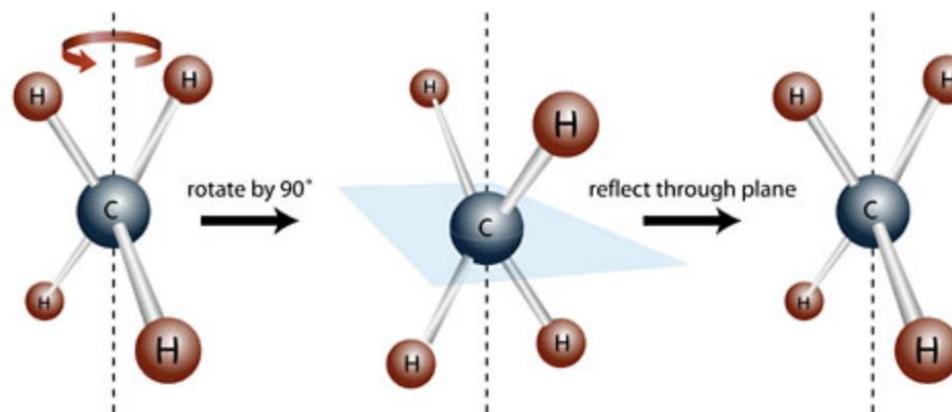
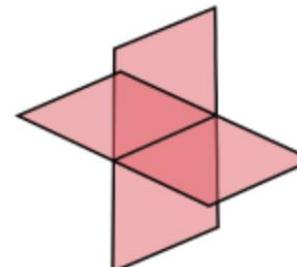
Transformation that leaves an object or structure unchanged in its overall appearance or properties

Improper Rotation: Mirror and Rotation

Symmetry Elements



Plane



Symmetries

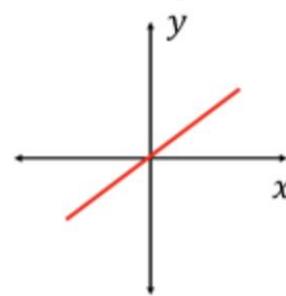
Transformation that leaves an object or structure unchanged in its overall appearance or properties

Glide Plane: Translation and Reflection

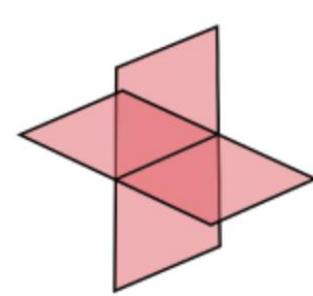
Screw axis : Rotation and Reflection

Symmetry Elements

Line

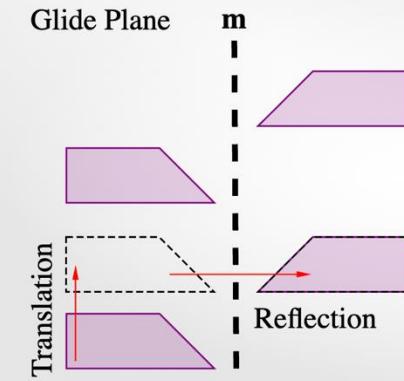


Plane

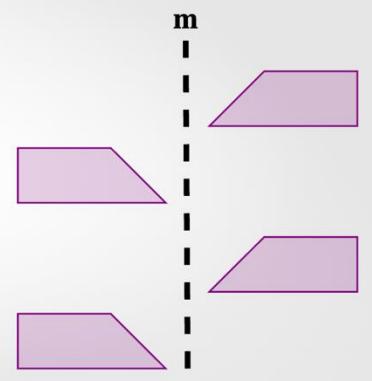


Glide Plane

m

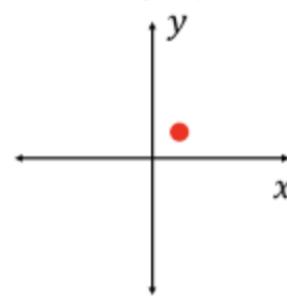


m

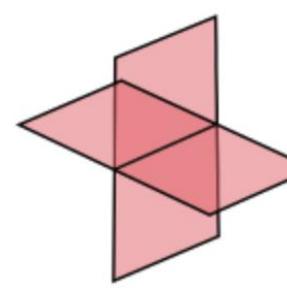


Symmetry Elements

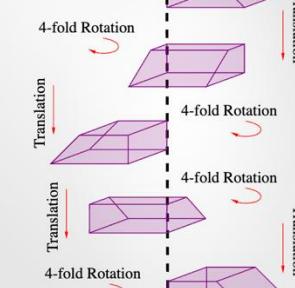
Point



Plane



Screw Axis
 4_1



Schoenflies Notation

- Used mainly in **molecular symmetry** and **group theory** (chemistry, spectroscopy, quantum mechanics).
- Each symbol refers to a **point group**: the set of all symmetry operations that leave at least one point fixed.

(a) Letters

- C_n : Cyclic group with an n -fold rotation axis.
- D_n : Dihedral group with an n -fold rotation axis and n perpendicular C_2 axes.
- S_n : Improper rotation axis, consisting of an n -fold rotation followed by reflection through a plane perpendicular to the axis.
- T : Tetrahedral symmetry (e.g., methane CH₄).
- O : Octahedral symmetry (e.g., SF₆).
- I : Icosahedral symmetry (e.g., buckminsterfullerene C₆₀).

(b) Modifiers

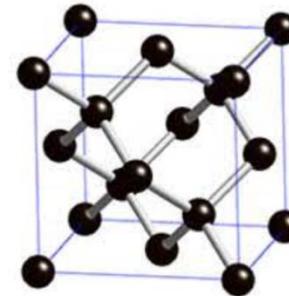
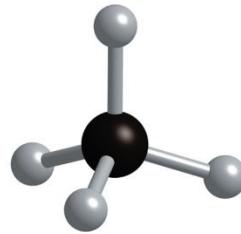
- h : Horizontal mirror plane (σ_h), perpendicular to the principal axis.
- v : Vertical mirror plane (σ_v), containing the principal axis.
- d : Dihedral mirror plane, bisecting the angle between two C_2 axes.
- i : Inversion center.

**• 32 crystallographic point groups
That can be represented using
Schoenflies Notation**

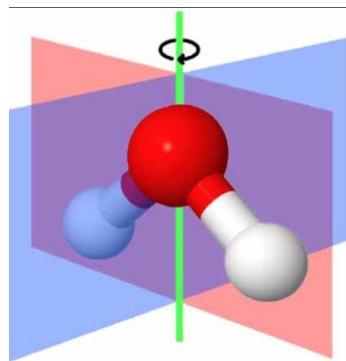
Schoenflies Notation

- Examples

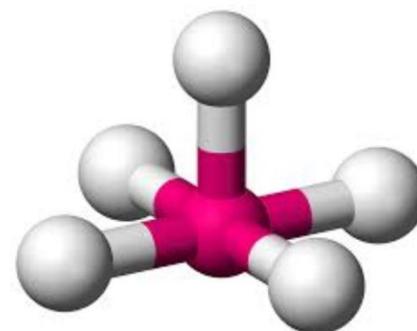
T_d = Methane, Diamond



C_{2v} = Water

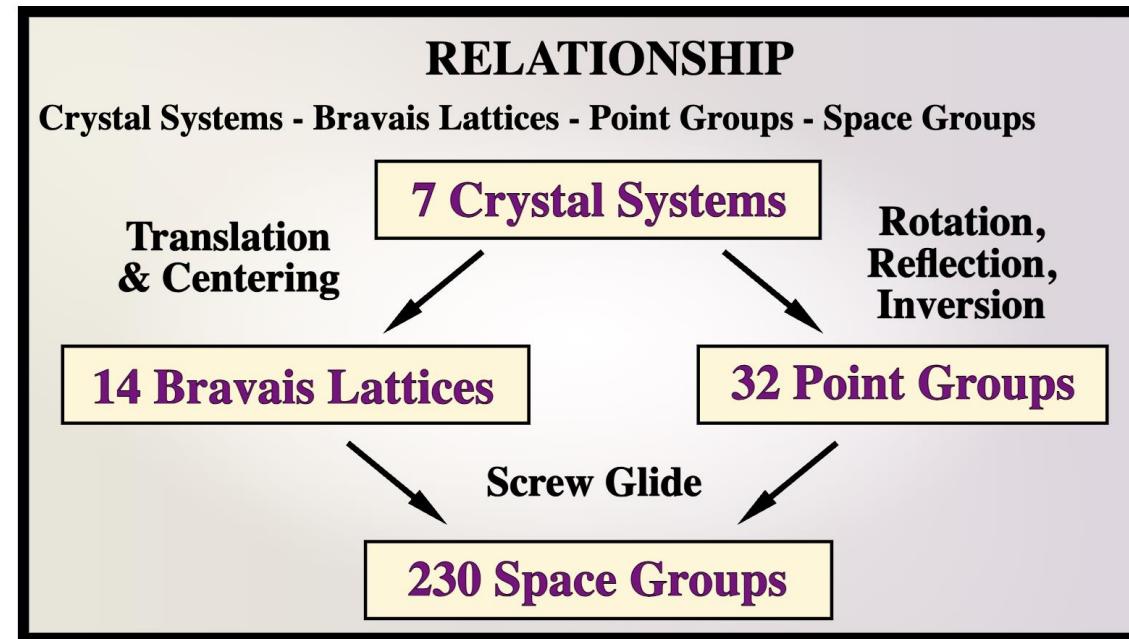


C_{4v} = Square pyramidal molecules (e.g. XeO_4)



Point Groups and Space Groups

A point group is a group of symmetry operations *that leave at least one point fixed*. That means no overall translations (you don't slide the structure). They include rotations, reflections, inversion, roto-inversion.



You may wonder then, why are there only 230 space groups? Although $14 \text{ Bravais lattices} \times 32 \text{ point groups} = 448$, several of those resulting 448 space groups are duplicates of each other. After removing duplicates, we end up with 230 space groups.

Hermann–Mauguin (International) Notation

Space groups (230 groups): point operations plus translations
(pure translations, screw axes nm, glide planes a, b, c, n, d, sometimes e);
begins with a lattice centering symbol.

A. Lattice centering (space groups only)

P primitive	A, B, C base-centered (on the named face)
I body-centered	F face-centered (all faces)
R rhombohedral (hexagonal axes)	

B. Rotation and rotoinversion symbols (point & space)

1, 2, 3, 4, 6	proper n -fold rotation axes
1̄	inversion center
3̄, 4̄, 6̄	rotoinversion axes

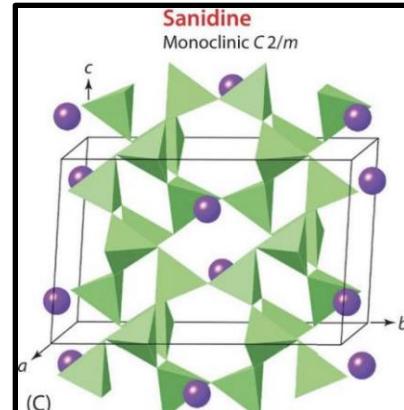
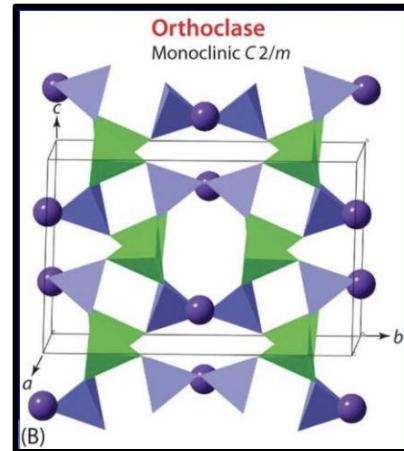
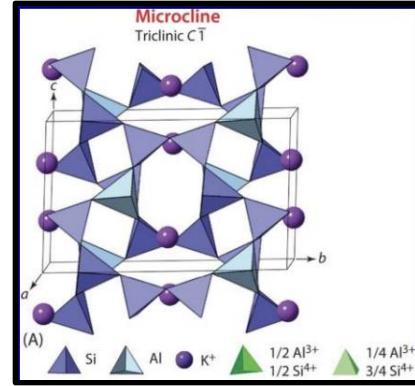
C. Mirrors and glides

m	mirror plane
a, b, c	glide plane with translation $\frac{1}{2}$ along lattice vector a, b, c
n	glide with diagonal $\frac{1}{2}(\mathbf{a} + \mathbf{b})$ type translation
d	diamond glide (e.g. in Fd $\bar{3}m$)
e	double-glide (appears in specific orthorhombic settings)

Hermann–Mauguin (International) Notation

1. System & lattice (P/A/B/C/I/F/R).
2. Principal axis (order and screw subscript if any).
3. Horizontal mirror/glide after slash /.
4. Vertical mirrors/glides (orthorhombic: three letters for $\perp a, b, c$).
5. Consistency with allowed groups in that system.

Symbol	Element	Meaning
Numbers ($n = 1, 2, 3, 4, 6$)		n-fold rotation axis. Example: 4 = 4-fold rotation (90).
$\bar{1}$		Inversion center. Each point (x, y, z) maps to $(-x, -y, -z)$.
Overbar (\bar{n})		Rotoinversion axis (rotation + inversion). Examples: 2 (mirror plane), $\bar{3}$ (3-fold rotoinversion), $\bar{4}$, 6.
m		Mirror plane. Reflection through a plane.
$/m$		Mirror plane perpendicular to a rotation axis. Example: $4/m$.
Subscript numbers (n_k)		Screw axes: n -fold rotation + translation along the axis. Examples: 2_1 (180 + 1/2 translation), $3_1, 3_2, 4_1, 4_2, 4_3, 6_1$ to 6_5 .
a, b, c		Glide planes with translation along the a , b , or c crystallographic axis.
n (glide)		Diagonal glide plane: translation along half a face diagonal.
d (diamond glide)		Diamond glide plane: diagonal translation typical of fcc lattices.
Combinations (e.g., 222, mm2, mmm)		Indicate the coexistence of multiple rotation and/or mirror elements. Example: 222 = three perpendicular 2-fold axes, mmm = three mutually perpendicular mirror planes.

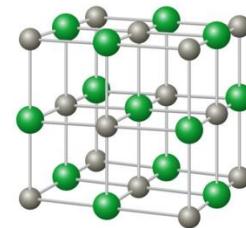


Hermann–Mauguin notation (also known as international notation) does not uniquely identify a crystal.

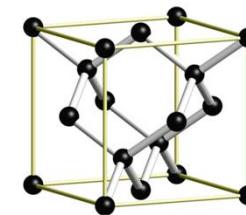
Hermann–Mauguin (International) Notation

No.	HM Symbol	Explanation of Notation	Simple Crystal Example
1	Fm–3m	*F* = facecentred cubic lattice; *m3m* = mirror planes + 3fold rotoinversion + full cubic symmetry elements.	NaCl (rocksalt / halite) (No.225).
2	Fd–3m	*F* = facecentred cubic; *d* = diamond glide; *3m* as above (rotointerversion + mirrors).	Diamond-carbon (C) (No.227).
4	Pm–3m	*P* = primitive cubic; *m3m* same symmetry core (mirrors + rotointerversion) without extra centring.	CsCl structure (No. 221).
5	I4/mmm	*I* = bodycentred tetragonal; *4* = 4fold rotation axis; *mmm* = mirror planes in perpendicular directions.	Ti ₂ Cu (No.139).

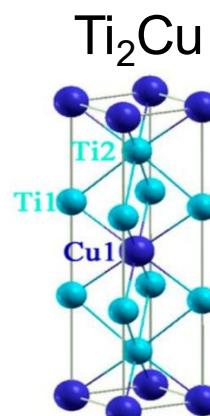
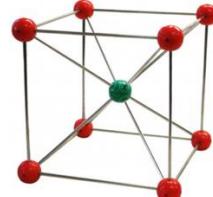
NaCl



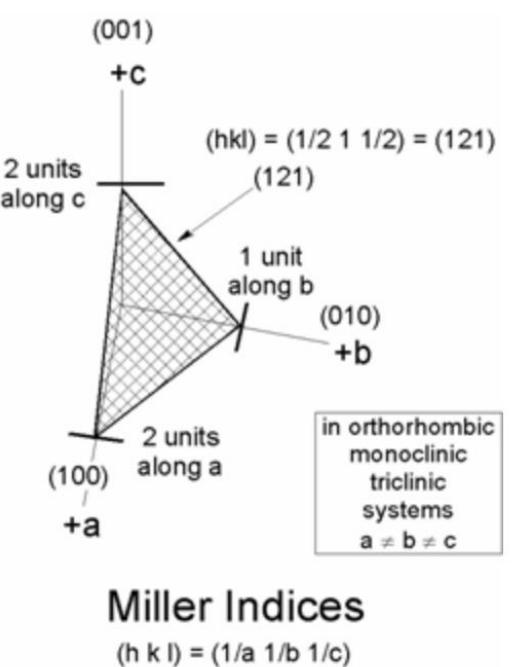
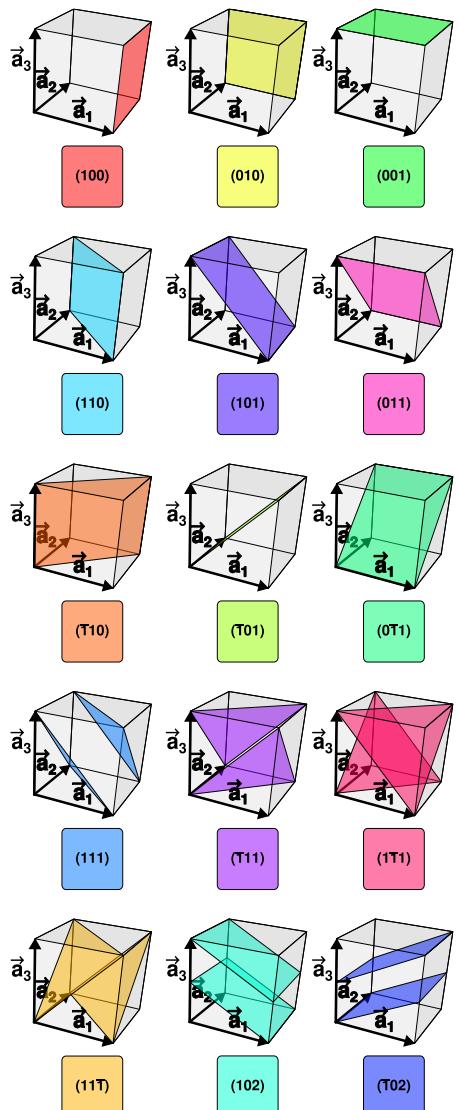
C-Diamond



CsCl



Directions in Crystals



Procedure to define Miller indices (hkl) of a crystal plane:

- Determine the intercepts of the plane with the crystallographic axes in terms of lattice constants (a, b, c)
- Take the reciprocals of these intercepts
- Clear fractions to obtain smallest set of integers .

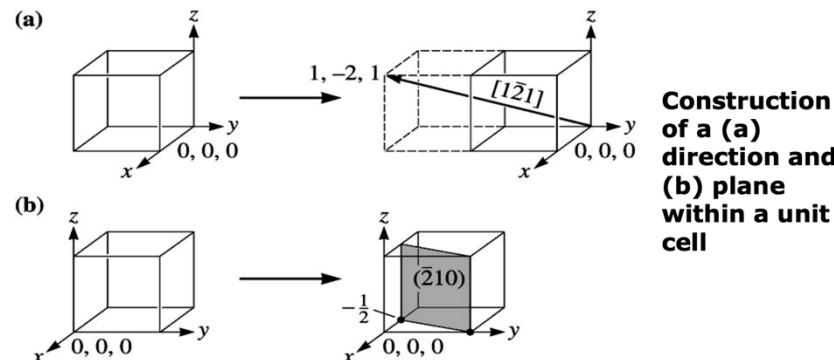
Enclose the result in parentheses (hkl) . Example: A plane cuts the x, y, z axes at (a, ∞, ∞) $\Rightarrow (100)$ plane.

Why we need Miller indices: To describe the orientation of planes and directions in crystals . Essential for diffraction , electronic band structure, slip systems , etc. Provide a compact integer notation instead of long vector equations

Surfaces, or planes through the crystal, can be described by first considering the intercepts of the plane along the a , b , and c axis used to describe the lattice.

Interplanar spacing

Draw (a) the $[1\bar{2}1]$ direction and (b) the $[\bar{2}10]$ plane in a cubic unit cell.



**Construction
of a (a)
direction and
(b) plane
within a unit
cell**

One characteristic of a crystal that can be determined is the distance between nearest equivalent parallel planes. Another characteristic is the surface concentration of atoms, number per square centimeter ($\#/cm^2$), that are cut by a particular plane.

Definition: The interplanar spacing d_{hkl} is the perpendicular distance between parallel planes in a crystal, indexed by Miller indices (hkl) .

General formula (orthorhombic lattice):

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

where a, b, c are the lattice constants.

Special cases:

- **Cubic ($a = b = c$):**

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

- **Tetragonal ($a = b \neq c$):**

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

Interplanar spacing

Definition: The interplanar spacing d_{hkl} is the perpendicular distance between parallel planes in a crystal, indexed by Miller indices (hkl) .

General formula (orthorhombic lattice):

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

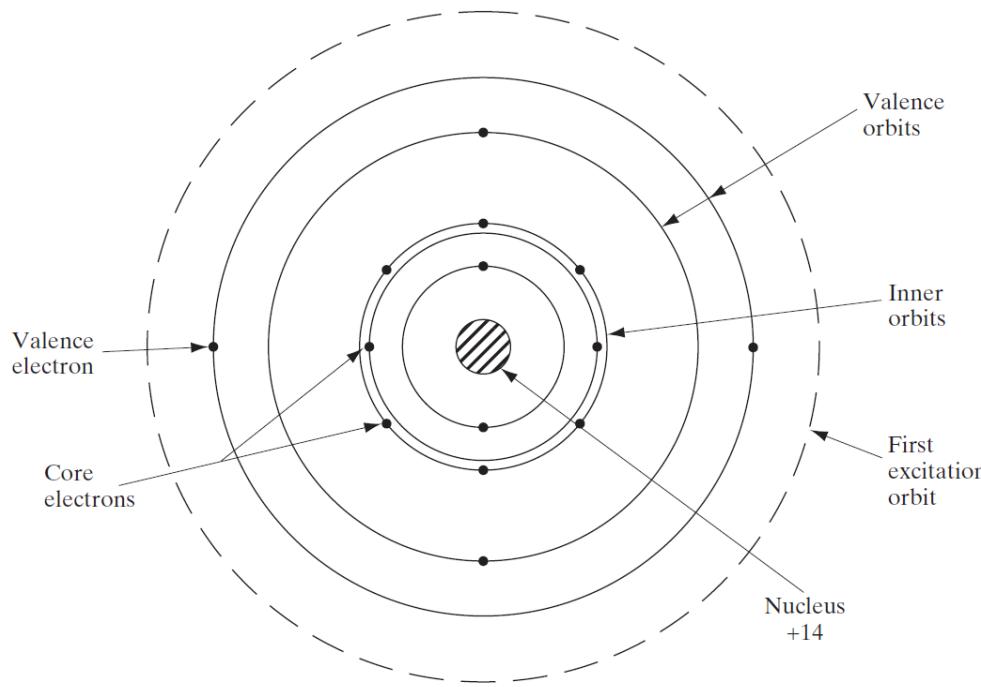
- The magnitude of the normal vector (in reciprocal space) is

$$|\vec{n}| = \sqrt{\left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2}.$$

- By the definition of reciprocal lattice vectors, the interplanar spacing is the inverse of this length:

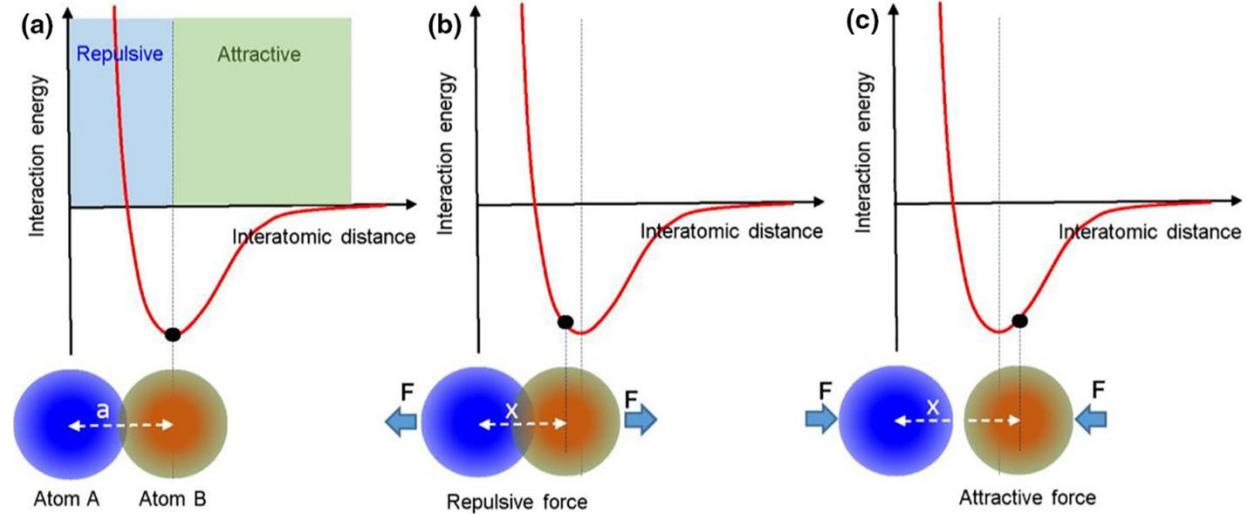
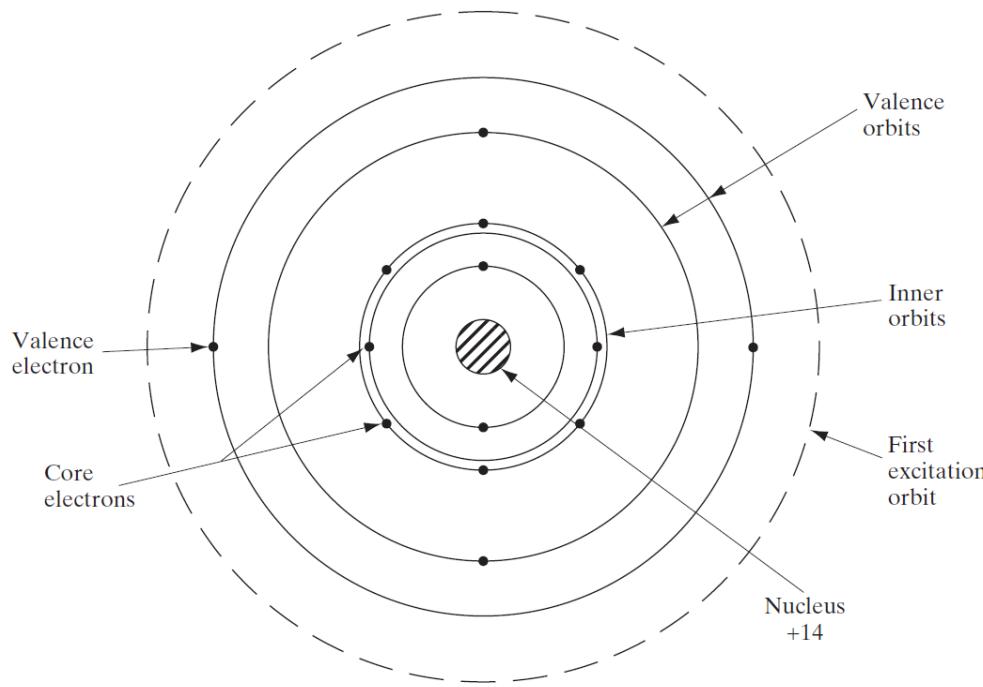
$$d_{hkl} = \frac{1}{|\vec{n}|}.$$

Bohr Model of Atoms



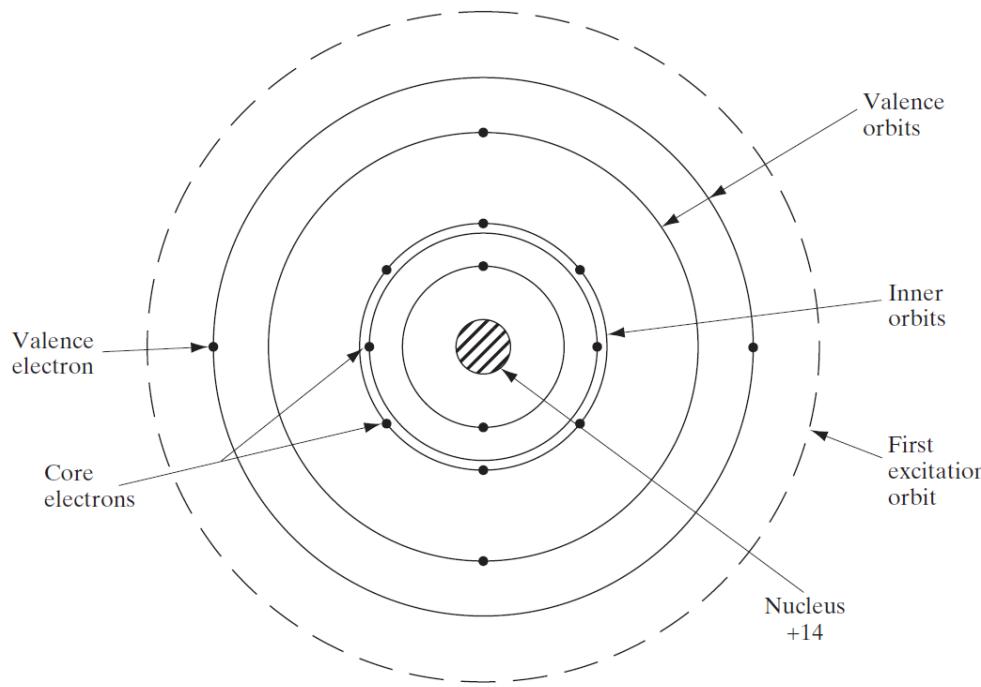
- Electrons move around the nucleus in orbits of well-defined radius.
- Issue: Classical electrodynamics predicts radiating, spiralling electrons \Rightarrow unstable atom
- Electrons orbiting in orbits do not interact with each other.
 - The energy of the electron depends on the principal quantum number n .
 - According to Planck's relation, when an electron moves from one orbit to another, it absorbs or emits radiation.

Bohr Model of Atoms



- **Energy minimisation:** In thermal equilibrium, atoms interact in such a way that the total energy of the system is as low as possible. If the interaction between atoms is not strong enough to lower the energy, they will not “stick together” to form a solid .

Bohr Model of Atoms



- It **breaks down for d- and f-block elements**, where available d- or f-orbitals expand the valence shell capacity beyond 8.
- Transition metals and inner transition metals obey more general rules (crystal field theory, ligand field stabilization, and relativistic effects) rather than the octet rule.

The **octet rule** is a guideline in chemistry and solid-state physics that explains how atoms tend to bond in order to achieve stability.

• **Statement:**

- Atoms tend to gain, lose, or share electrons until they have **eight electrons in their outermost (valence) shell**, which corresponds to the stable electron configuration of a noble gas.

Atomic Bonding

- **Bond strength and type dictate material properties.**

How Bonds and Crystal Structure Influence Properties

- **Hardness:**

- Stronger bonds generally result in harder crystals; for instance, the strong covalent bonds in diamond make it extremely hard.

- **Melting Point:**

- Crystals with strong interatomic forces, such as ionic and covalent networks, require more energy to break their bonds, leading to high melting points.

- **Brittleness vs. Ductility:**

- Ionic crystals are brittle because any shift can cause like charges to align and repel, shattering the crystal. Metallic structures, conversely, are ductile due to the ability of the electron sea to allow atoms to slide past each other without breaking bonds.

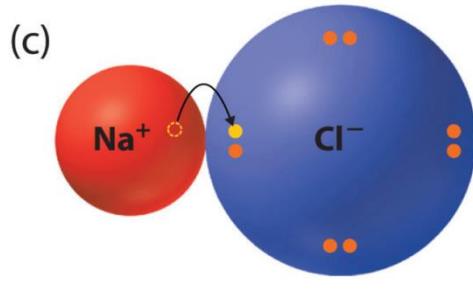
- **Geometric Shape:**

- Crystals exhibit well-defined, flat faces and regular shapes because atoms arrange themselves in a repeating, periodic pattern, forming a stable, low-energy crystal lattice.

Atomic Bonding

1. Ionic Bonding

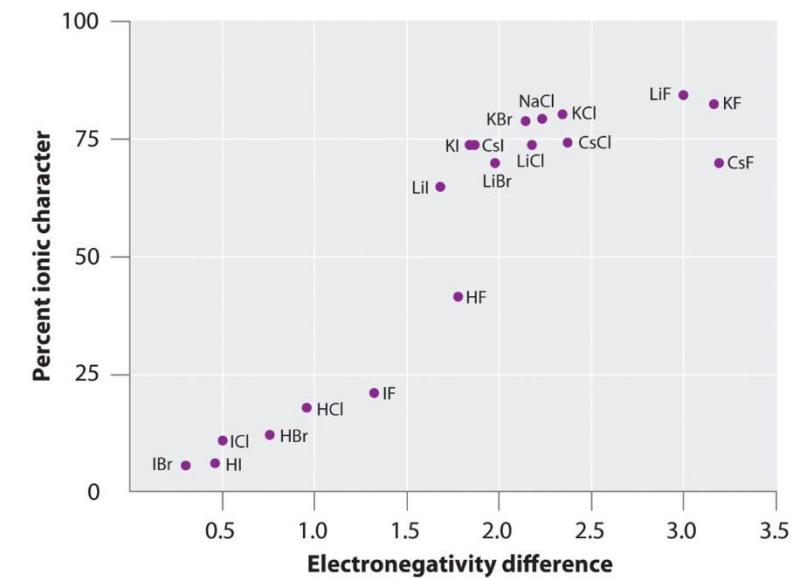
2. Occurs between atoms of very different electronegativities (e.g. NaCl).
3. One atom donates an electron (cation), the other accepts (anion).
4. The resulting positive and negative ions are held together by strong Coulomb forces.
5. Properties: high melting point, brittle, good insulators because electrons are tightly bound.



Complete transfer of one or more valence electrons.
Full charges on resulting ions.

- Large difference in **electronegativity** between atoms (typically $\Delta\chi > \sim 1.7$ on the Pauling scale).
- One atom has low ionisation energy (alkali or alkaline earth metals).
- The other has high electron affinity (halogens, oxygen, etc.).
- **Example:** NaCl, MgO.

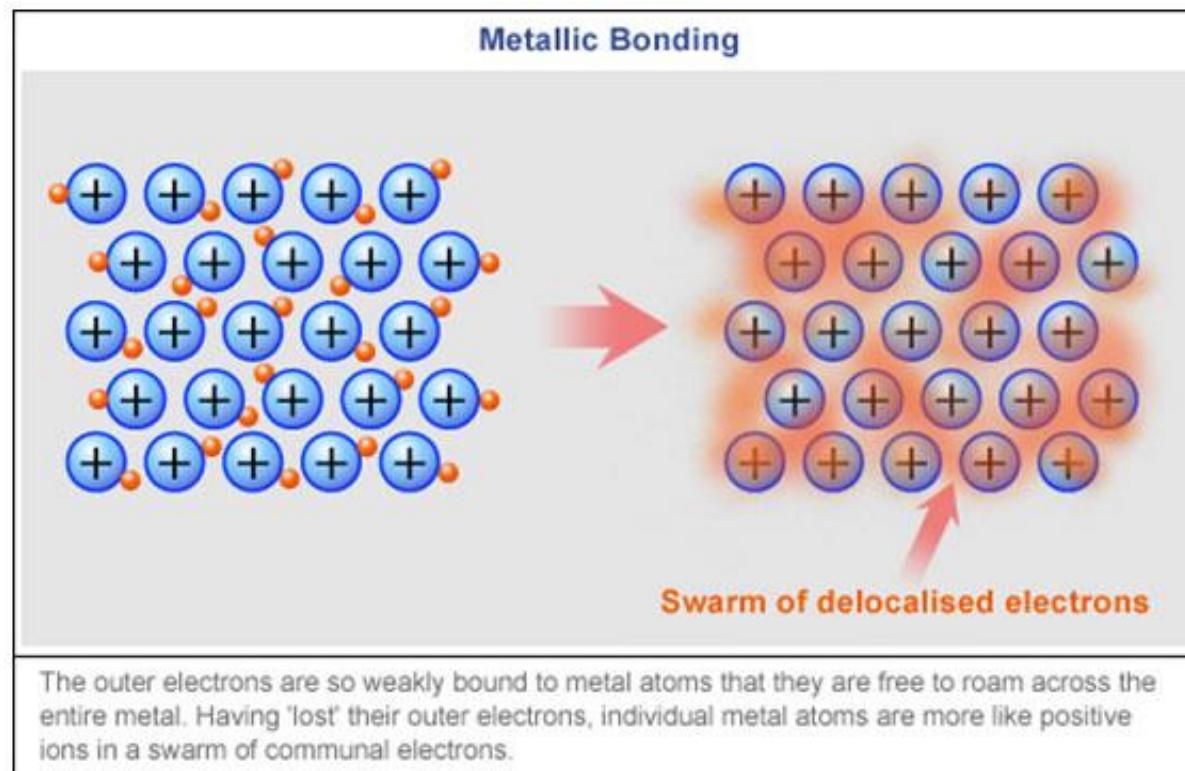
Occurs between metals (groups I/II) and non-metals (groups VI/VII).



Atomic Bonding

1. Metallic Bond

2. Occurs between atoms of very different electronegativities (e.g. NaCl).
3. One atom donates an electron (cation), the other accepts (anion).
4. The resulting positive and negative ions are held together by strong Coulomb forces.
5. Properties: high melting point, brittle, good insulators because electrons are tightly bound.



Atomic Bonding

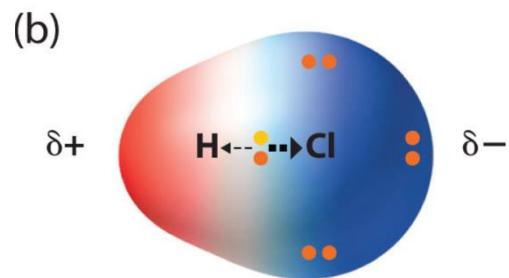
2. Covalent Bonding

3. Atoms share electrons in order to complete their outer shells.
4. Very common in semiconductors (e.g. Si, Ge, GaAs).
5. Each atom contributes one or more valence electrons to form directional bonds.
6. Properties: high hardness, relatively high melting point, can be insulators or semiconductors depending on band structure.



Nonpolar covalent bond

Bonding electrons shared equally between two atoms.
No charges on atoms.



Polar covalent bond

Bonding electrons shared unequally between two atoms.
Partial charges on atoms.

- Large difference in **electronegativity** between atoms (typically $\Delta\chi > \sim 1.7$ on the Pauling scale).
- One atom has low ionisation energy (alkali or alkaline earth metals).
- The other has high electron affinity (halogens, oxygen, etc.).
- **Example:** NaCl, MgO.

👉 Occurs between metals (groups I/II) and non-metals (groups VI/VII).c

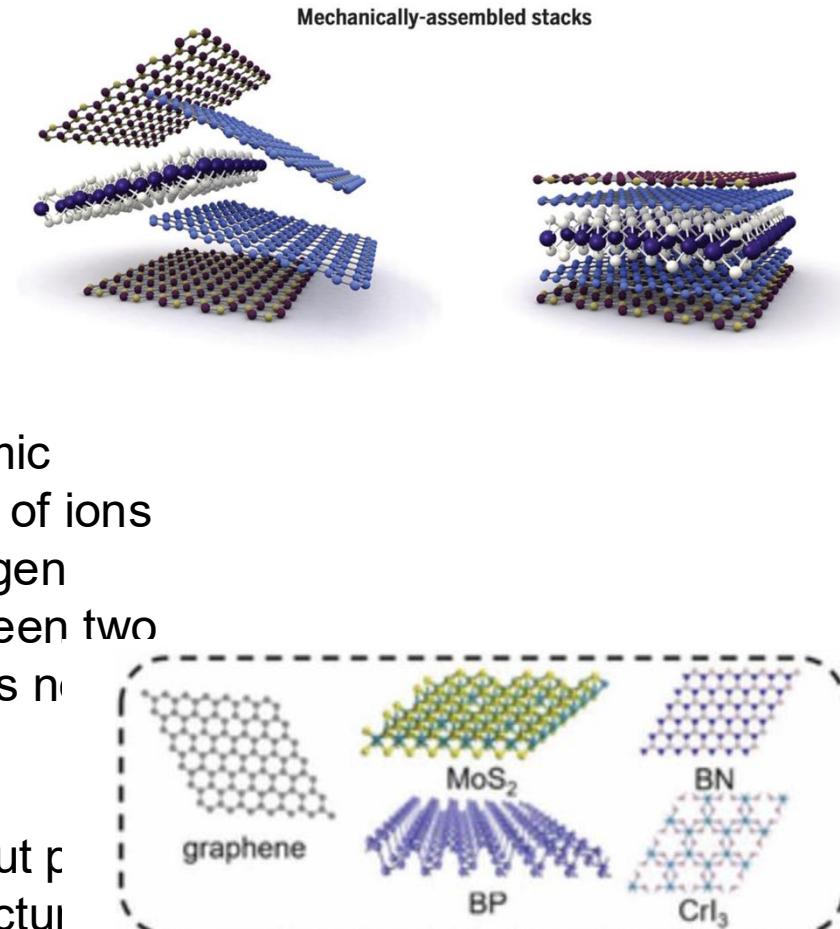
Atomic Bonding

1. Van der Waals forces

2. Occurs between atoms of very different electronegativities (e.g. NaCl).
3. One atom donates an electron (cation), the other accepts (anion).
4. The resulting positive and negative ions are held together by strong Coulombic forces.
5. Properties: high melting point, brittle, good insulators because electrons are delocalized.

are the residual attractive or repulsive forces between molecules or atomic groups that do not arise from a covalent bond, or electrostatic interaction of ions or of ionic groups with one another or with neutral molecules. Like hydrogen bonds, van der Waals forces rely on dipoles, a difference in charge between two molecules. But unlike hydrogen bonds the van der Waals dipole usually is non-permanent, but transient.

Van der Waals forces are relatively weak compared to covalent bonds, but play a fundamental role in fields as diverse as supramolecular chemistry, structural biology, polymer science, nanotechnology, surface science, and condensed matter physics. Van der Waals forces define many properties of organic compounds, including their solubility in polar and non-polar media.



Defects

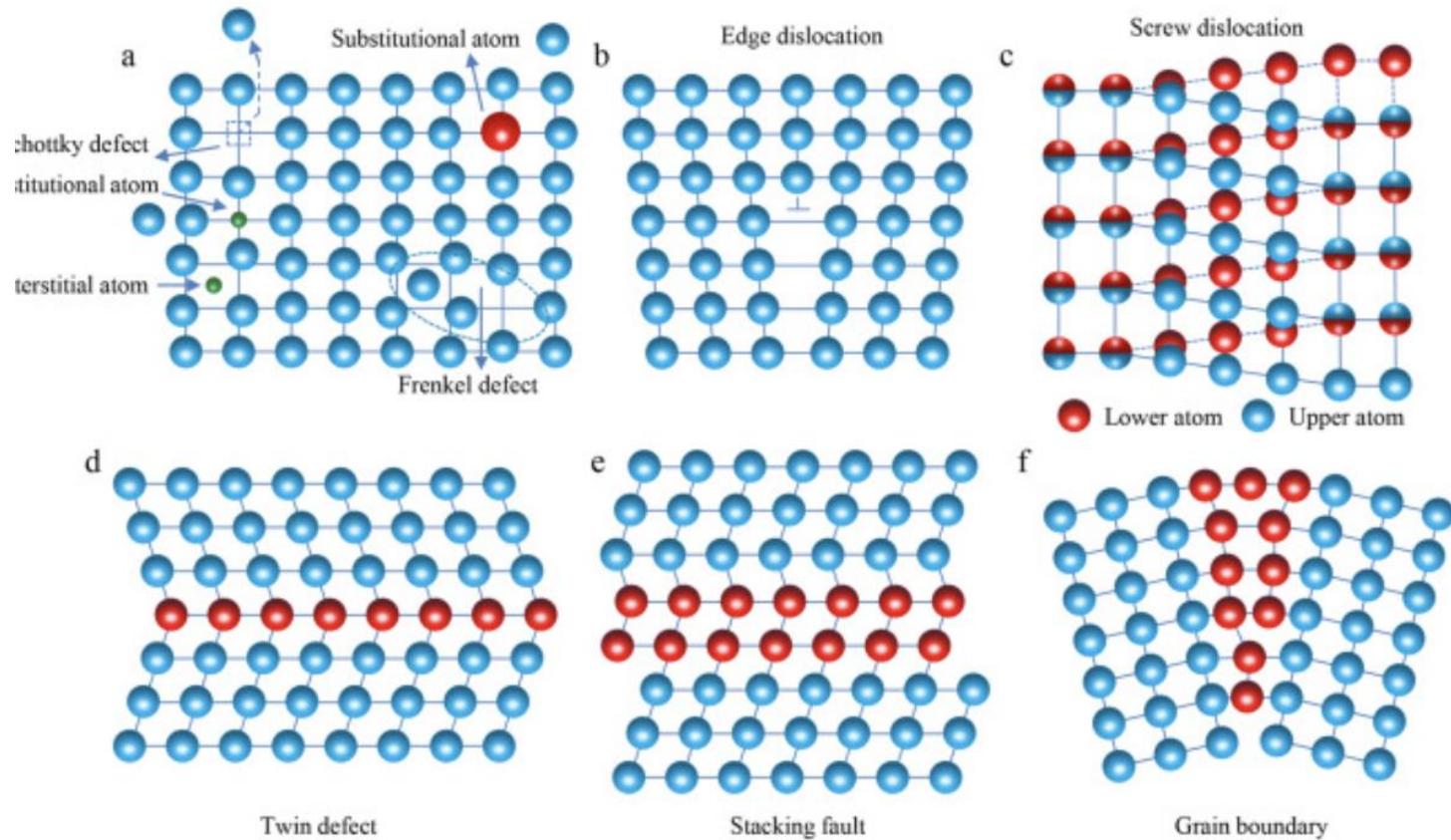
Imperfections tend to alter the electrical properties of a material and, in some cases, electrical parameters can be dominated by these defects or impurities.

Defects in solids are irregularities or distortions in the otherwise perfect, repeating arrangement of atoms in a crystalline structure. These imperfections can be classified into four types based on their dimensionality: point defects (0D), which are single-atom deviations; line defects (1D), or dislocations, that are linear irregularities; planar or surface defects (2D), such as grain boundaries; and volume or bulk defects (3D), which include pores and cracks.

Defects

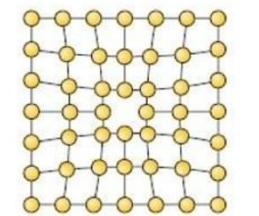
Irregularities or deviation from ideal arrangement of constituent particles around the point or atom in a crystalline solid is known as point defects.

Dislocations are linear defects around which some of the atoms of the crystal lattice are misaligned. There are two basic types of dislocations, the edge dislocation and the screw dislocation.

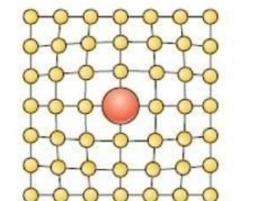


Defects

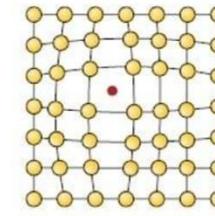
- **Vacancy:** increases electrical resistivity, enhances diffusion, lowers thermal conductivity
- **Interstitial:** increases hardness but decreases ductility; in semiconductors, can act as donors or recombination centres.
- If different in valence → introduces free carriers:
- Donors (n-type doping, e.g. P in Si).
- Acceptors (p-type doping, e.g. B in Si).
- Substitutional: foundation of semiconductor device operation; changes conductivity dramatically.
- Creates a **vacancy + interstitial pair**.
- **Frenkel Defect** : enhances ionic conductivity.
- **Schottky Defect:** A pair of vacancies optical absorption, important in laser crystals and photonics.



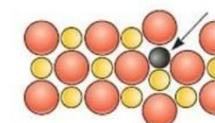
Vacancy



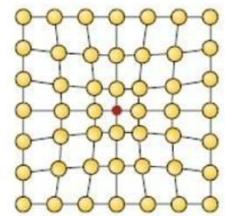
Large substitutional



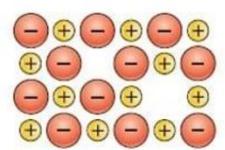
Interstitial



Frenkel defect



Small substitutional atoms



Schottky defect

Defects

$$c_v = \frac{n_v}{N} = \exp\left(-\frac{\Delta G_f}{k_B T}\right).$$

$$\Delta G_f = \Delta H_f - T\Delta S_f,$$

we can rewrite the concentration as

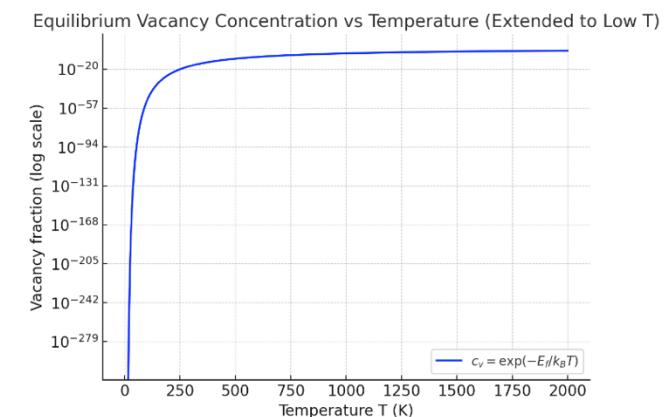
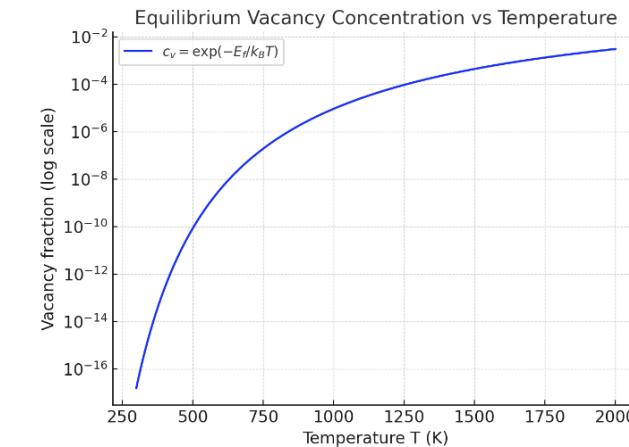
$$c_v = \exp\left(\frac{\Delta S_f}{k_B}\right) \exp\left(-\frac{\Delta H_f}{k_B T}\right).$$

If ΔS_f is small or approximately constant, the dominant contribution is

$$c_v \approx \exp\left(-\frac{\Delta H_f}{k_B T}\right) = \exp\left(-\frac{E_f}{k_B T}\right),$$

where E_f is the vacancy formation energy.

$$c_v = \exp\left(-\frac{E_f}{k_B T}\right),$$



Arrhenius Relations Limits

$$c_v = \frac{n_v}{N} = \exp\left(-\frac{\Delta G_f}{k_B T}\right).$$

1. Low temperature limit ($T \rightarrow 0$)

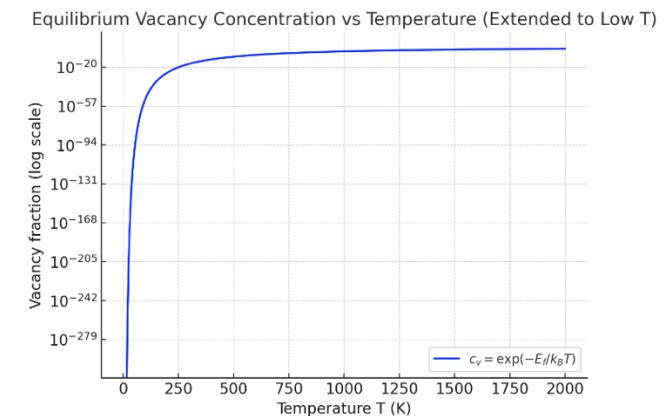
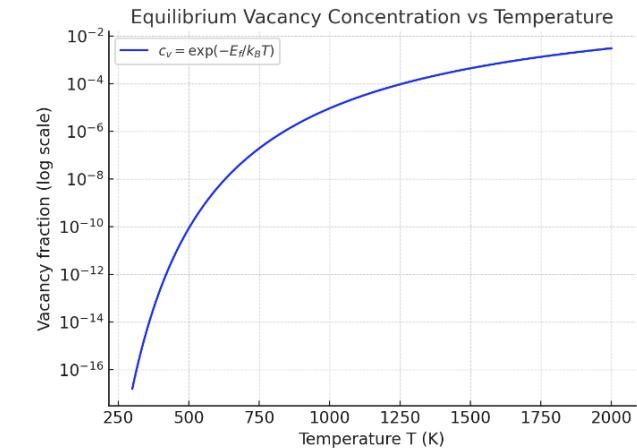
- Exponential term $\exp(-E_f/k_B T) \rightarrow 0$.
- Predicts essentially no defects.
- In reality: zero-point motion or non-equilibrium defects (quenched-in during growth) can exist, but these are not captured.
- Thus at very low T , the formula underestimates defect concentration.

2. High temperature limit ($T \rightarrow \infty$)

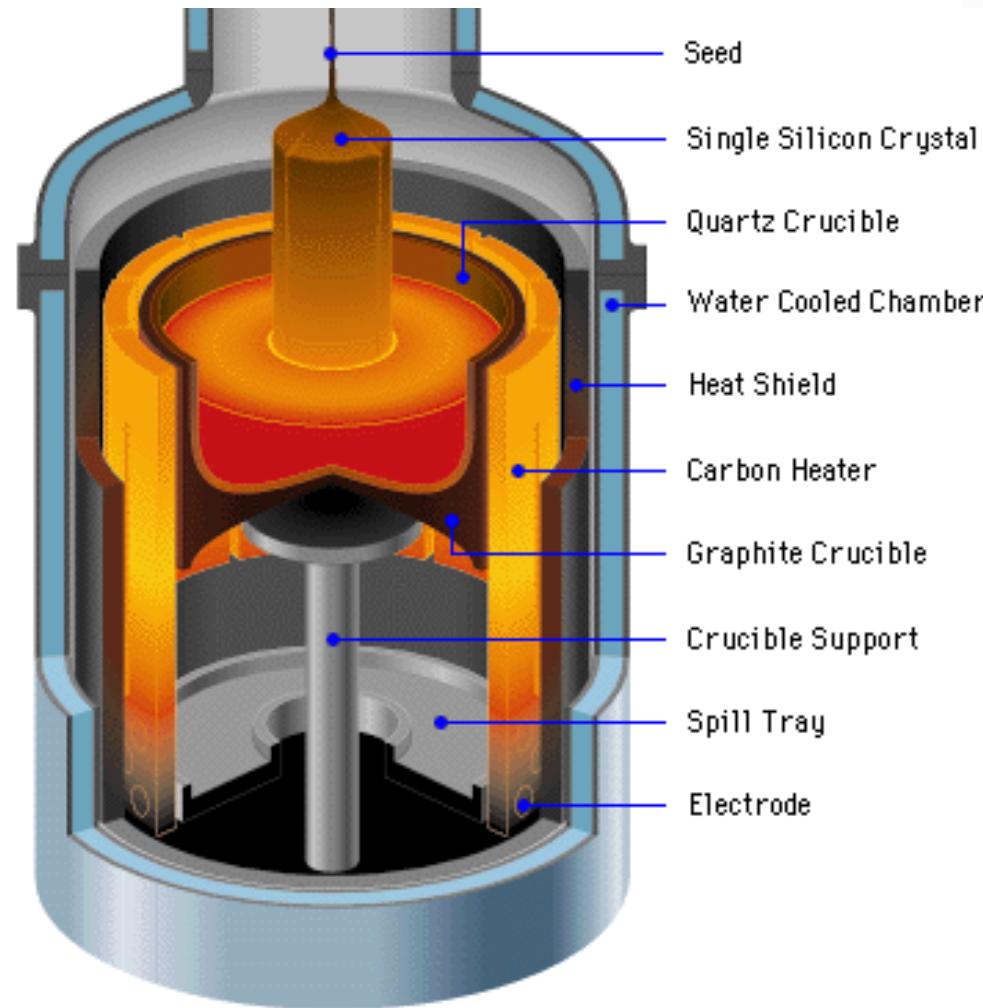
- The exponential term $\rightarrow 1$, so $n_d \rightarrow N$.
- That would mean "every site is defective", which is unphysical because the crystal lattice breaks down (melts) before this happens.
- Near melting, the approximation of independent defects fails: interactions, defect-defect clustering, and anharmonic effects become important.

3. Intermediate regime (valid range)

- The relation is accurate when $k_B T \ll E_f$ but not so small that n_d is immeasurable.
- Typically works well in the temperature window where the crystal is thermodynamically stable but defects are present in equilibrium concentrations (e.g. a few hundred °C up to well below melting).

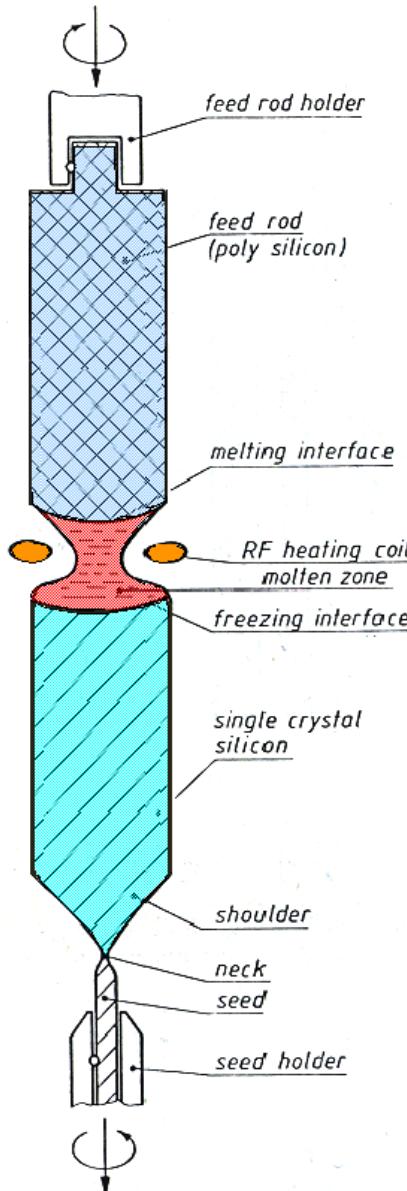


Bulk Single Crystal: Czochralski (CZ) Crystal Growth



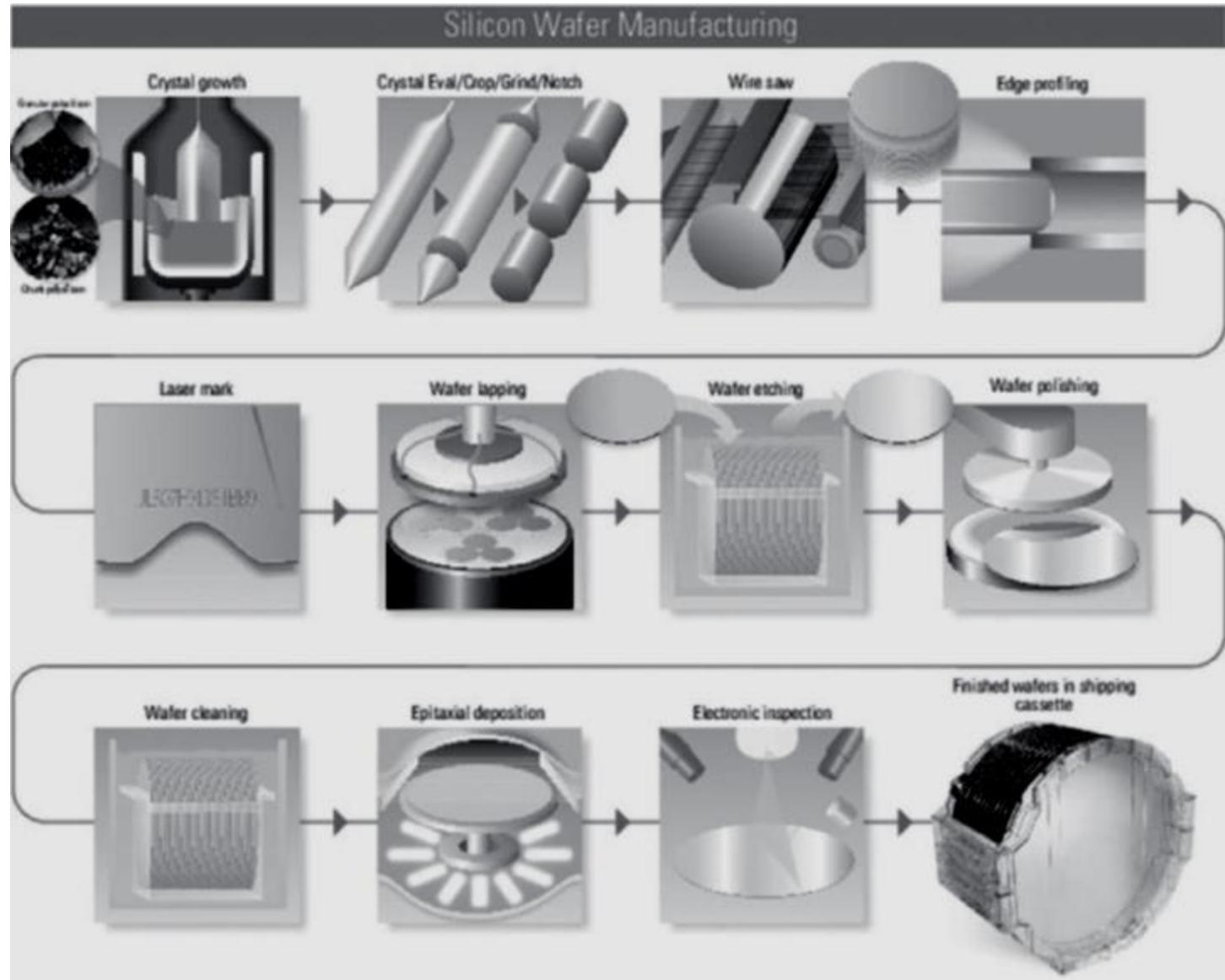
- Pure polycrystalline Silicon is placed into crucible
- Furnace heated to $>1420\text{ }^{\circ}\text{C}$
- Seed (single crystal) is inserted into the melt
- Seed rotates counter-clockwise, crucible rotates clockwise
- Seed is slowly withdrawn (a few mm/min): crystal diameter controlled by melt temperature and seed lift rate

Bulk Single Crystal: Float Zone (FZ) Crystal Growth



- ✓ Start with a seed at one end
- ✓ Impurities isolate into the molten zone and molten zone is moved along the crystal
- ✓ Superior purity over CZ material, especially oxygen contamination is reduced
- ✓ High-power, high-voltage, optical terahertz applications
- :(Molten zone held only by surface tension, hence ingot diameter <15 cm
- :(Radial distribution of dopants in FZ wafer not as uniform as in CZ wafer

Wafers



Epitaxial Growth

The growth of a thin crystal layer on a wafer of a compatible crystal substrate.

Classification:

- Homoepitaxy:
substrate-film: the same materials
- Heteroepitaxy:
substrate-film: different but similar materials

Methods:

- Vapor Phase Epitaxy
Chemical Vapor Deposition
- Molecular Beam Epitaxy

