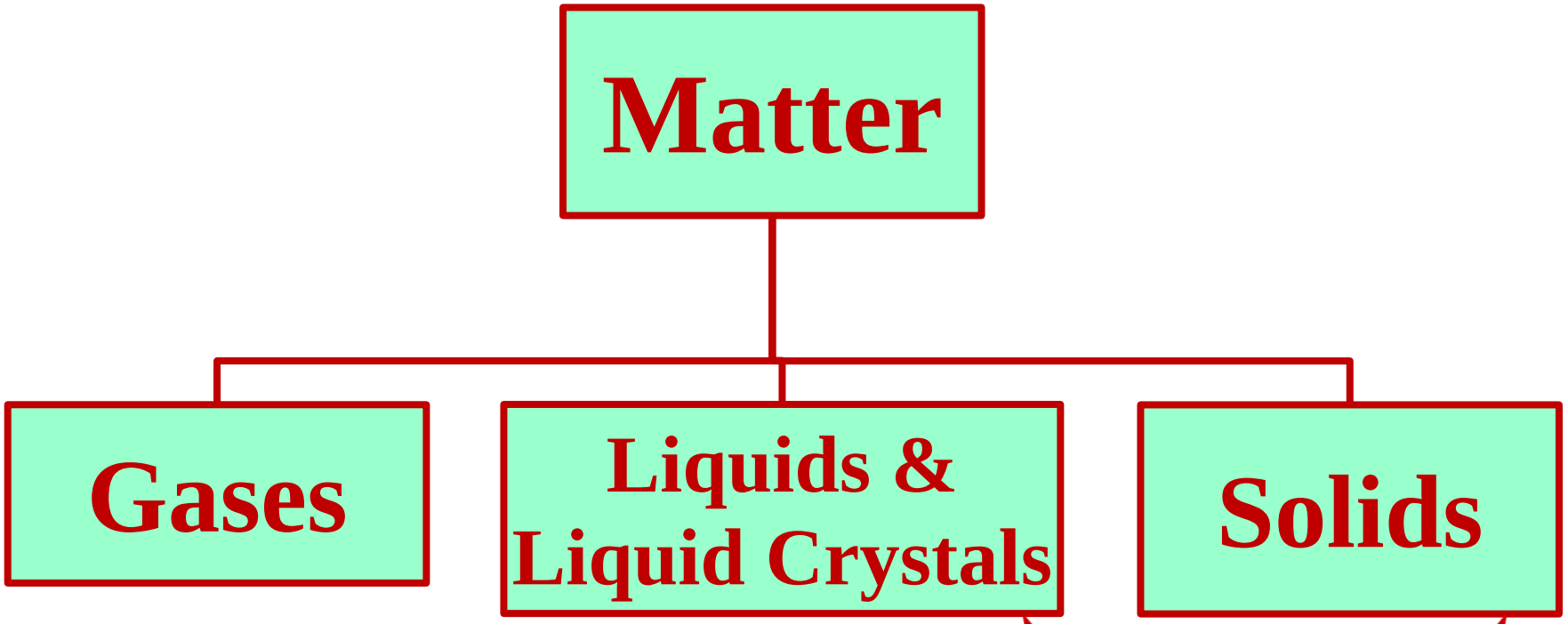
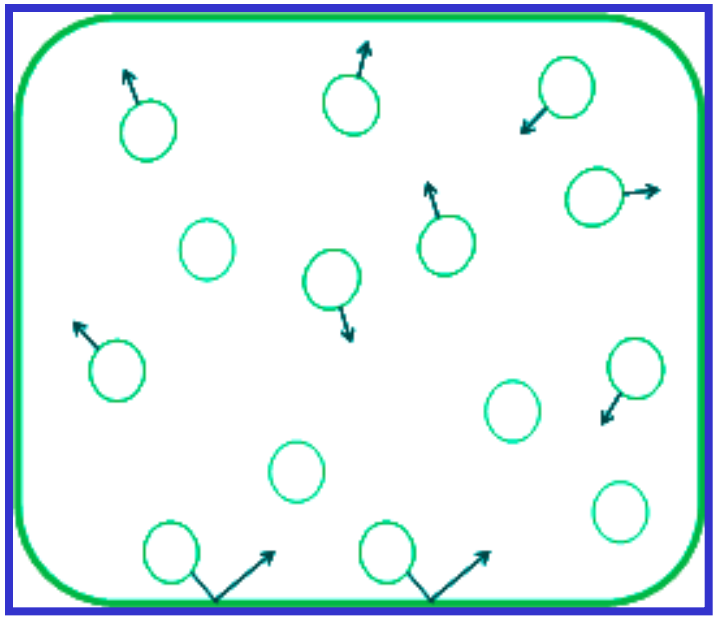


"**Condensed Matter**" includes ***both of these.***

Our focus is ***Solids!***

Gases

- ***Gases*** have atoms or molecules that do not bond to one another in a range of pressure, temperature & volume. Also, these molecules have no particular order & they move freely within a container.



Liquids

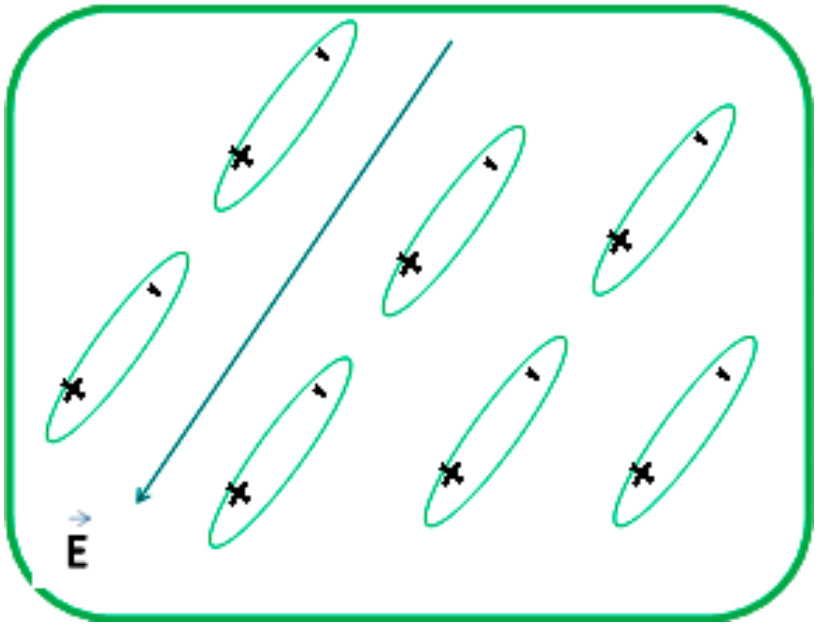
- Similar to gases, ***Liquids*** have no atomic or molecular order & they assume the shape of their containers.

- Applying low levels of thermal energy can easily break the existing weak bonds.

Liquid Crystals

- ***Liquid Crystals*** have mobile molecules, but a type of long range order can exist. The moalecules have a permanent electric dipole.

- Applying an electric field rotates the dipoles & establishes order within the collection of molecules.



Solids

- ***Solids*** consist of atoms or molecules ***undergoing thermal motion*** about their equilibrium positions, which are at ***fixed points*** in space.

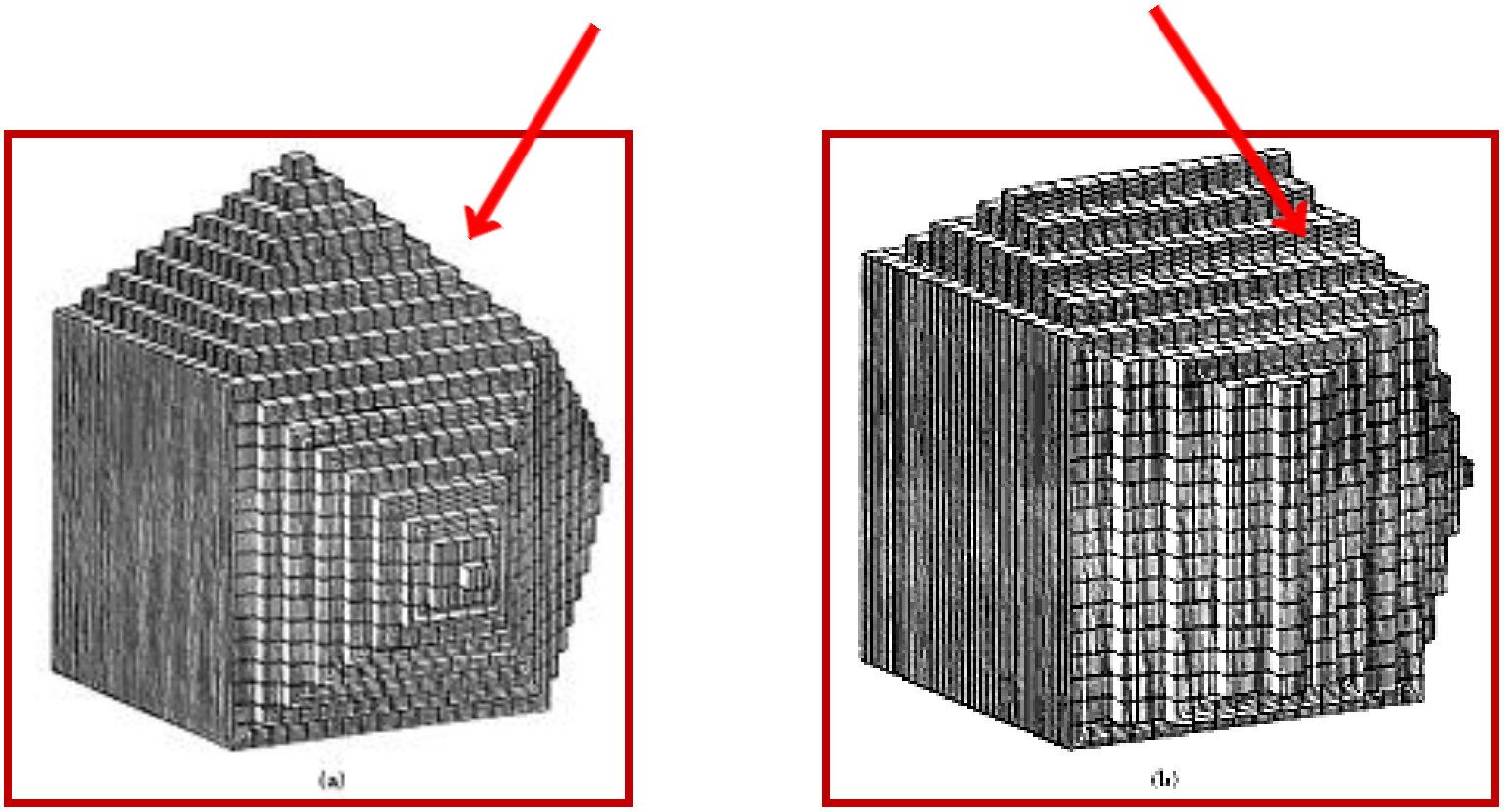
- ***Solids*** can be **crystalline**, **polycrystalline**, or **amorphous**.

- ***Solids*** (at a given temperature, pressure, volume) ***have stronger interatomic bonds*** than liquids.

- So, ***Solids*** ***require more energy*** *to* ***break the interatomic bonds*** than liquids**.**

Periodic Arrays of Atoms

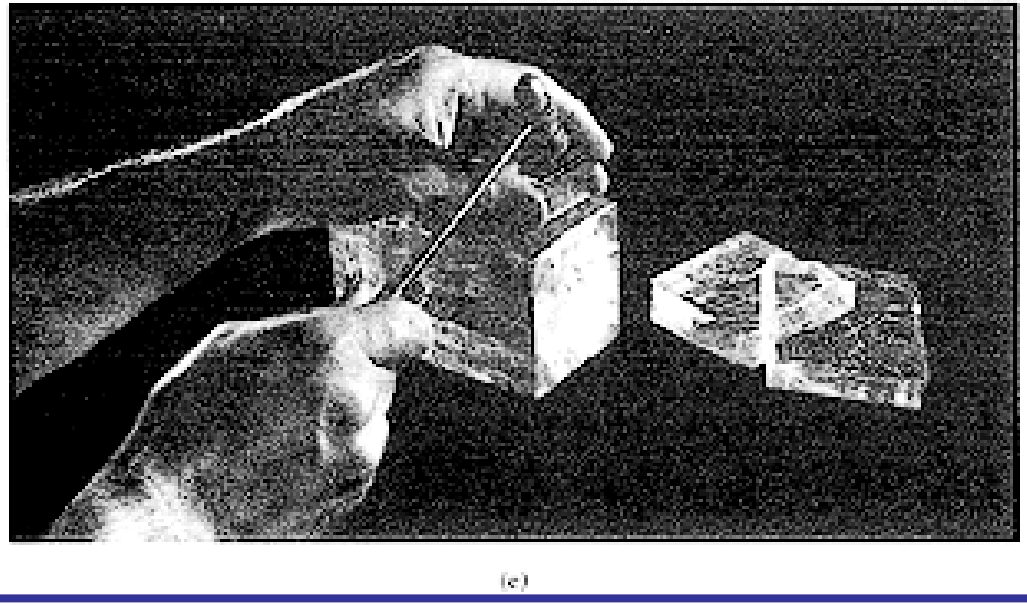
- The external appearance of crystals gives some clues.
- The figure shows that when a crystal is cleaved, we can see that it is built up of identical “building blocks”.



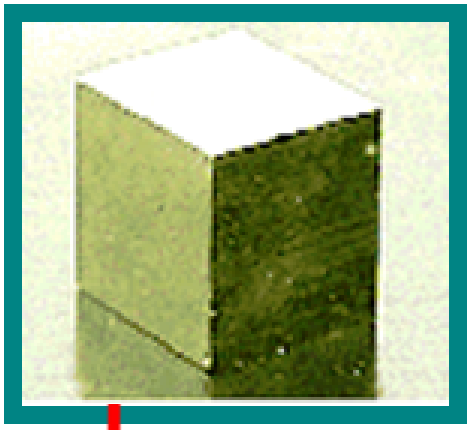
Experimental Evidence of periodic structures.

- The early crystallographers noted that the index numbers that define plane orientations are exact integers.

Cleaving a Crystal



Elementary Crystallography



Solid Material Types

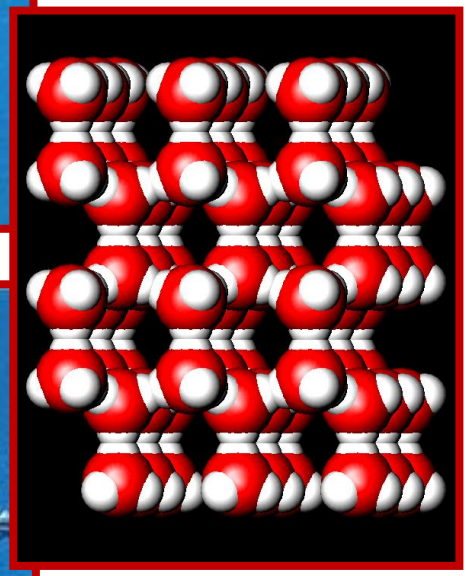
Crystalline

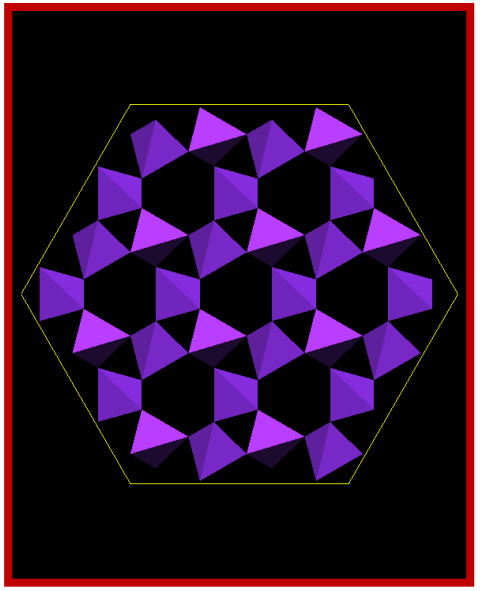
Polycrystalline

Amorphous

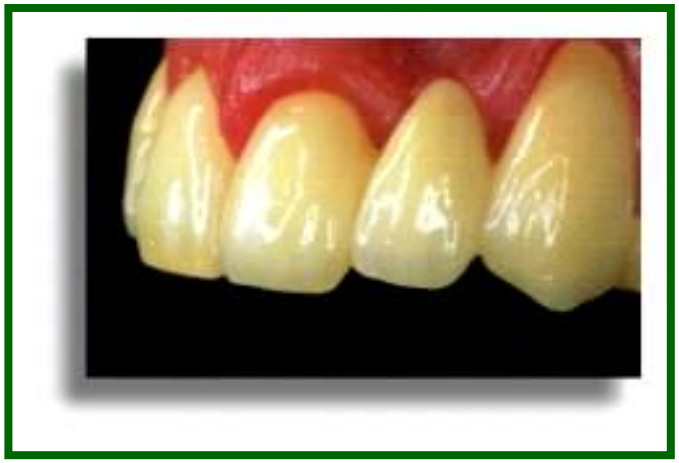
Single Crystals

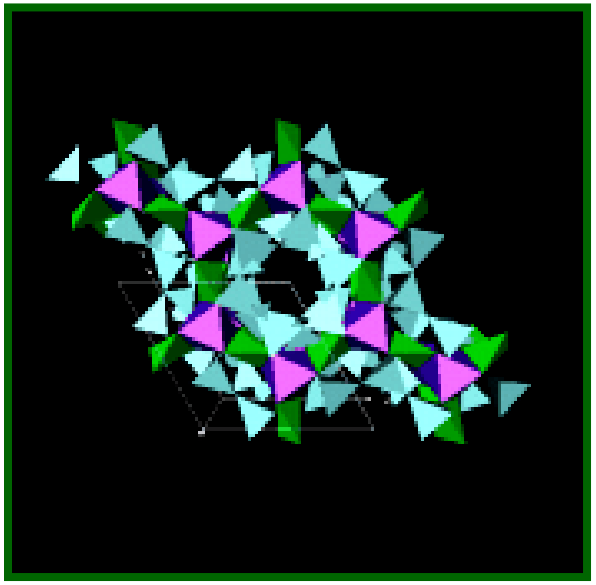
Crystals are Everywhere!

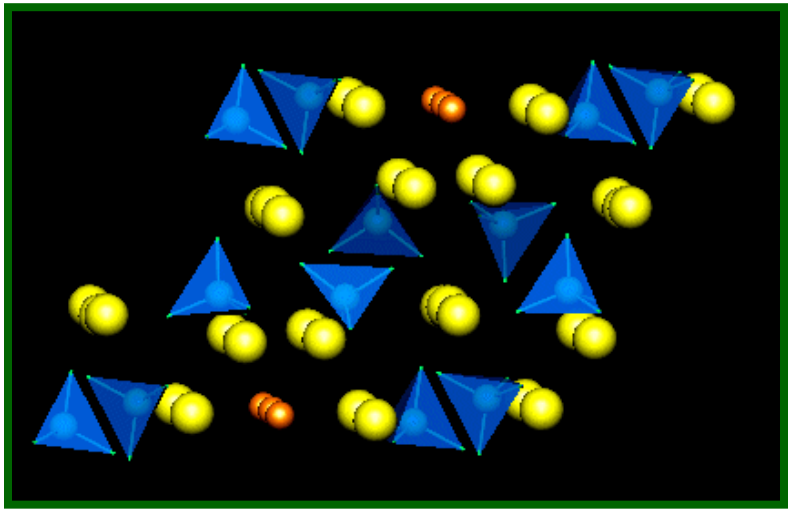




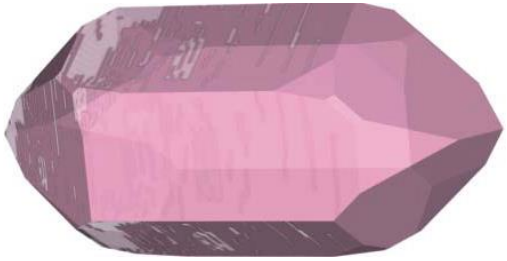
Crystals

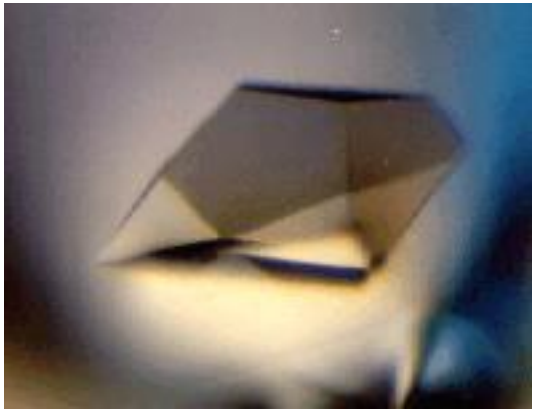


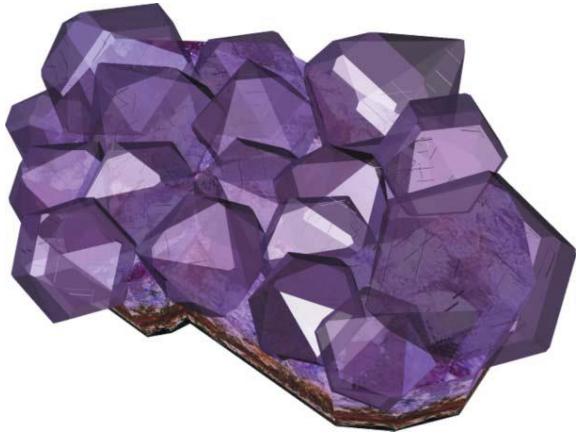




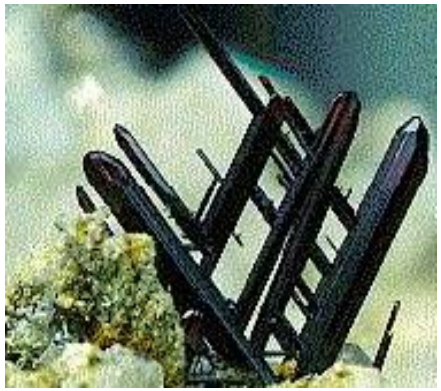
Crystals







Crystals



Crystals

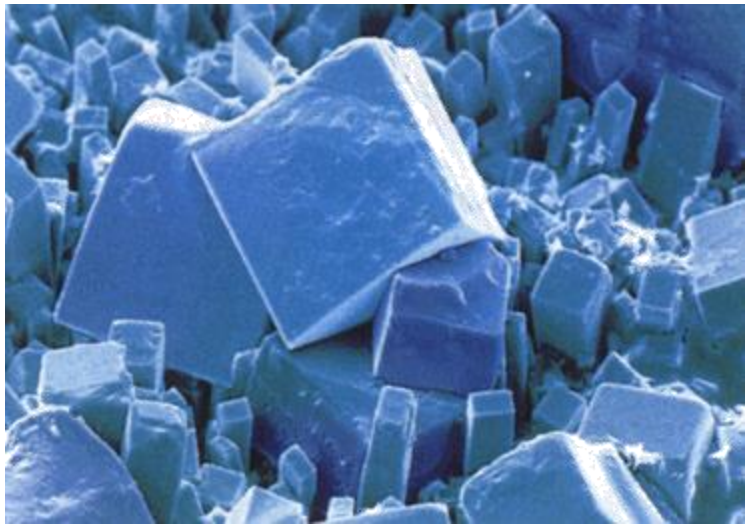
- A ***crystal*** or ***crystalline solid*** is a solid material whose constituent atoms, molecules, or ions are ***arranged in an orderly, repeating pattern extending in all three spatial dimensions*.**

- ***All crystals are solids, but all solids are not crystalline****!*

Crystallography

- **Crystallography** ≡ A branch of science dealing with the geometric description of crystals & their internal arrangements.

- It is also the science of crystals & the math used to describe them.

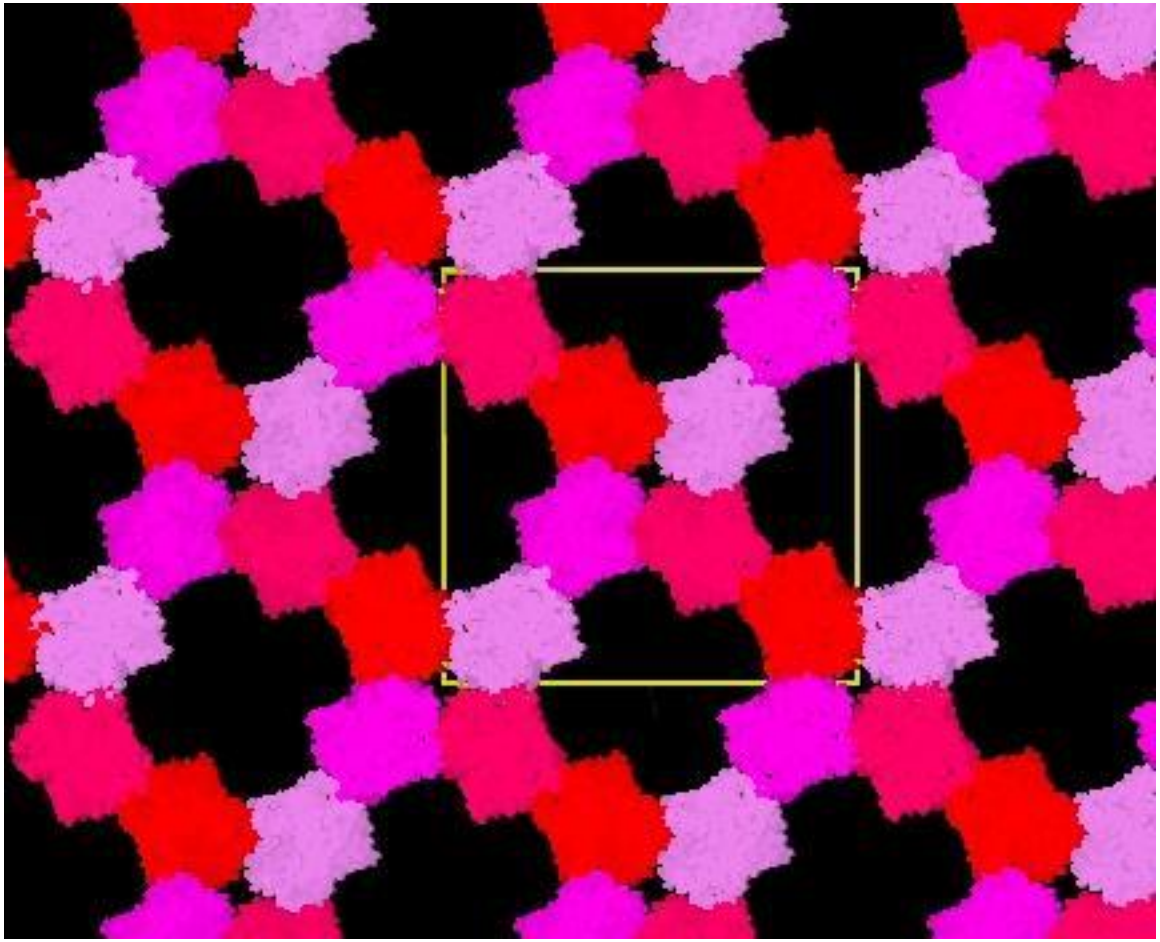


Crystallography

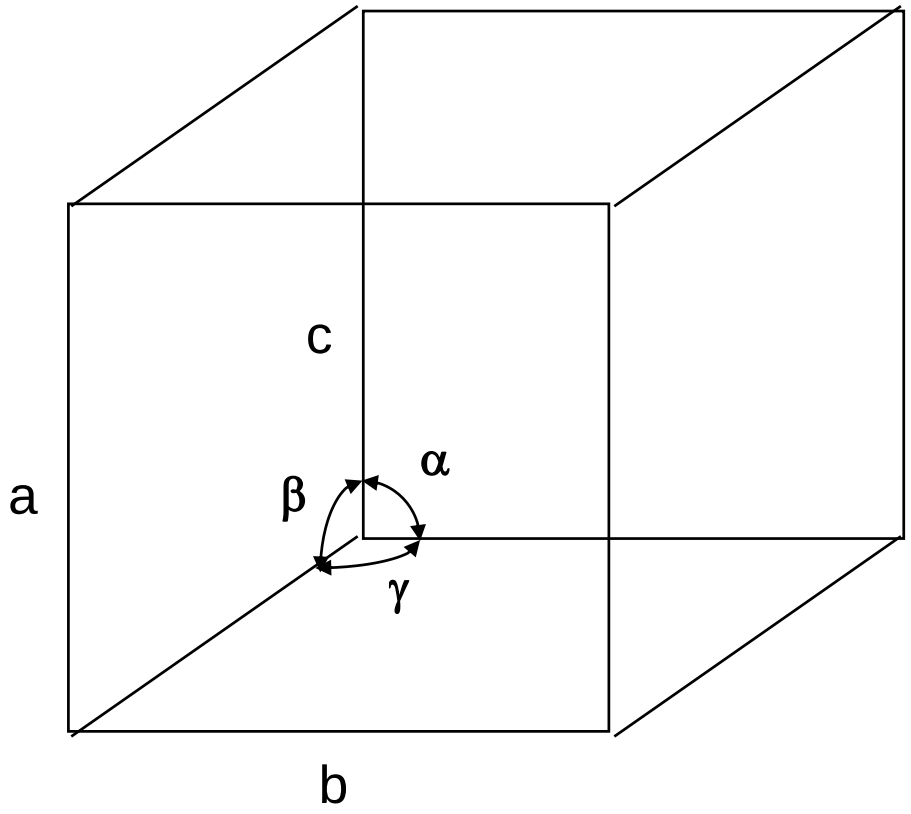
- These early studies led to the correct idea that crystals are regular three-dimensional arrays (***Bravais lattices***) of atoms and molecules.

- A single ***unit cell*** is repeated indefinitely along three principal directions that are not necessarily perpendicular.

The Unit Cell Concept



Unit Cell Description in Terms of Lattice Parameters



- **a ,b,** & **c** define the edge lengths & are referred to as the **crystallographic axes**.
- The angles between these are **a, b,** & **g**.
- The lattice parameters **a ,b, c, a, b,** & **g** give the dimensions of the unit cell.

The *Three General Types* of Solids

Single Crystal, Polycrystalline, Amorphous

- Each type is characterized by the size of the ordered region within the material. An ordered region is a spatial volume in which atoms or molecules have a regular geometric arrangement or periodicity.

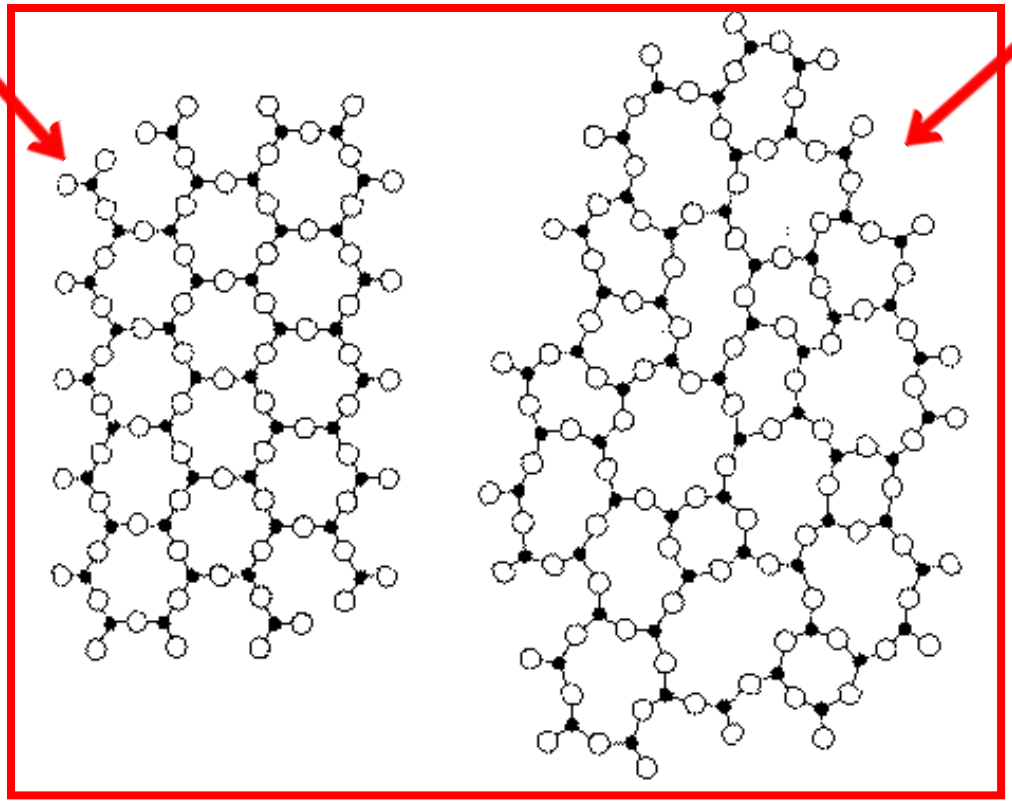
All Solids

- All solids have “resistance” to changes in both shape and volume.
- Solids can be **Crystalline or Amorphous**
- ***Crystals*** are solids that **consist of a periodic array of atoms, ions, or molecules**
  - If this periodicity is preserved over “large” (macroscopic) distances, the solid has **“Long-range Order”**
- **Amorphous solids** do not have **Long-Range Order**, but they often have **Short Range Order**

Solids

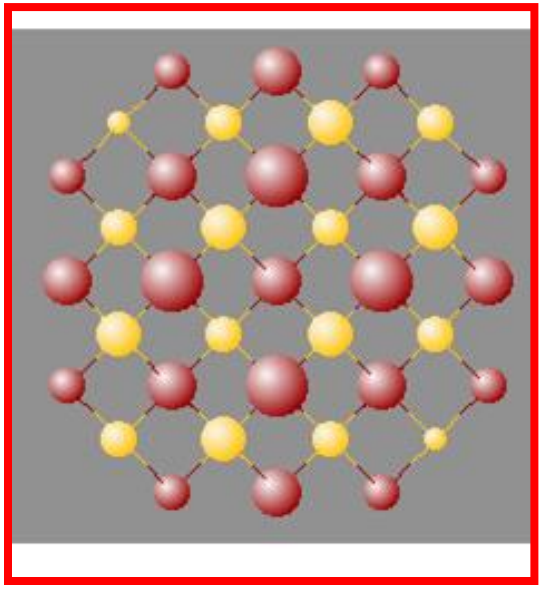
- **Crystals**:
  Short-range Order
  Long-range Order

- **Amorphous solids:**
  ~Short-range Order
  No Long-range Order



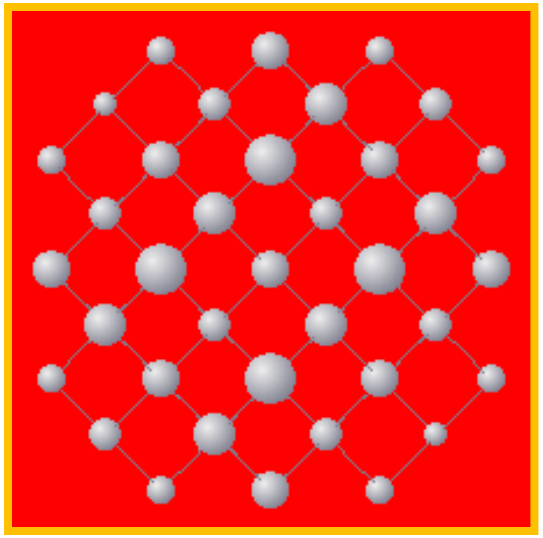
Solids

- **Different solids** can have the **same geometrical arrangements** of atoms
- **Their *Properties are determined by their crystal structure*: Both *crystal lattice* & *basis* are important**



Examples:

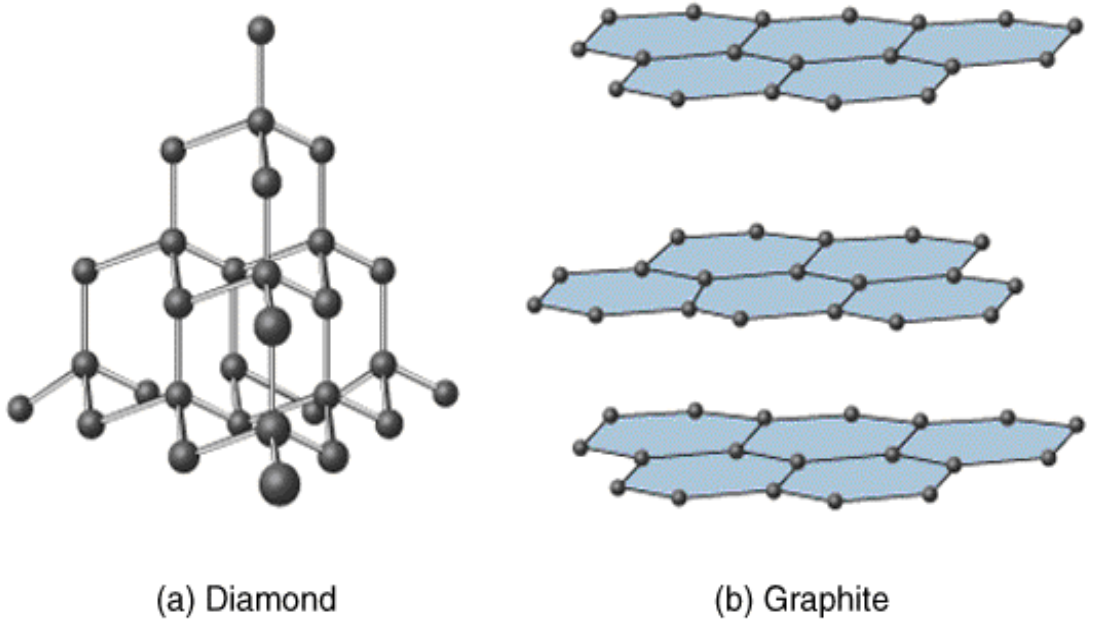
- **Si, Diamond (C), GaAs, ZnSe** all have the same lattice geometry
- **Si and C (Diamond)** Form the **"Diamond Structure"**
- **GaAs** and **ZnSe** form a structure called the **"Zinc Blende" Structure**



Solids

- Different arrangements of atoms (even the same atoms) can result in very different solid state properties

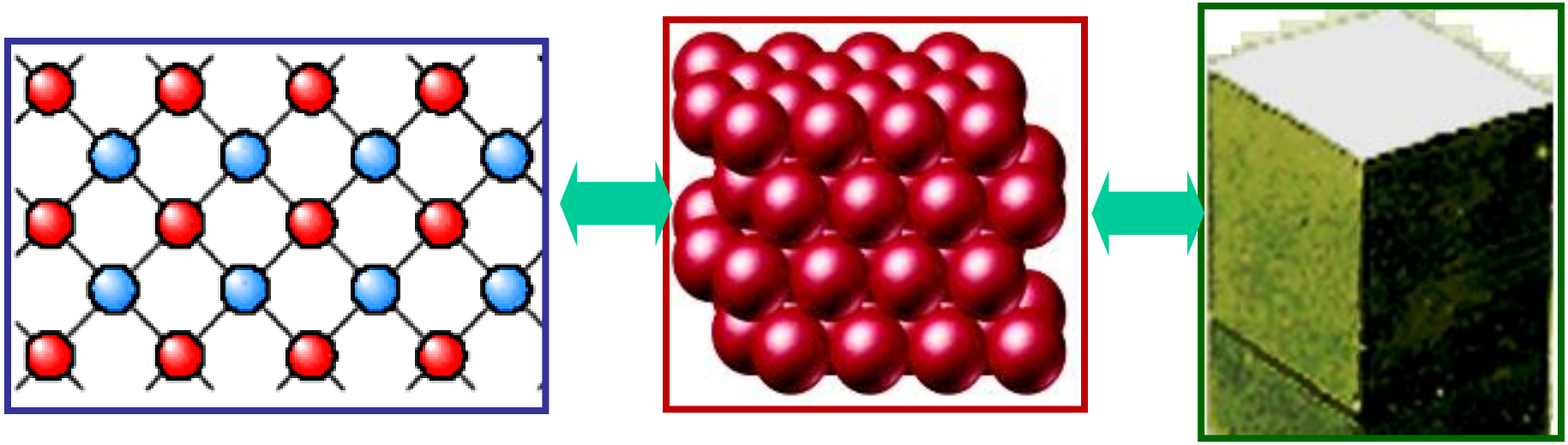
2 *very different* solids made of *only carbon* (C) atoms!



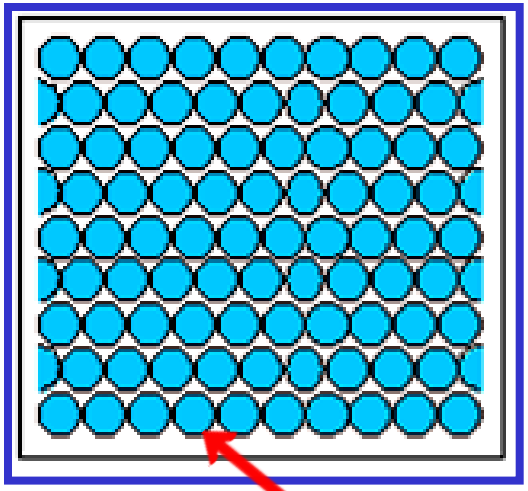
Crystalline Solids

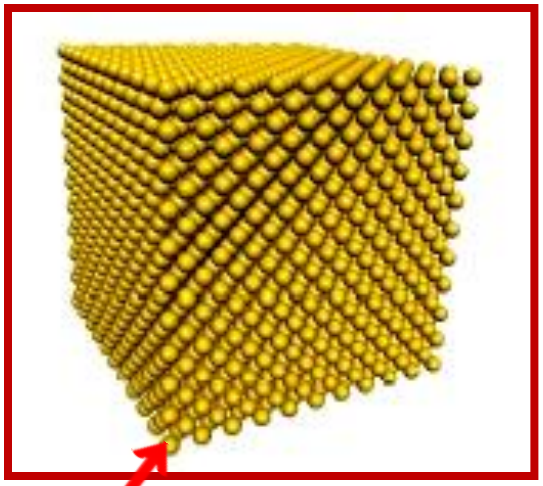
- A ***Crystalline Solid*** is the solid form of a substance in which the ***atoms or molecules*** are arranged in a definite, repeating pattern in three dimensions.

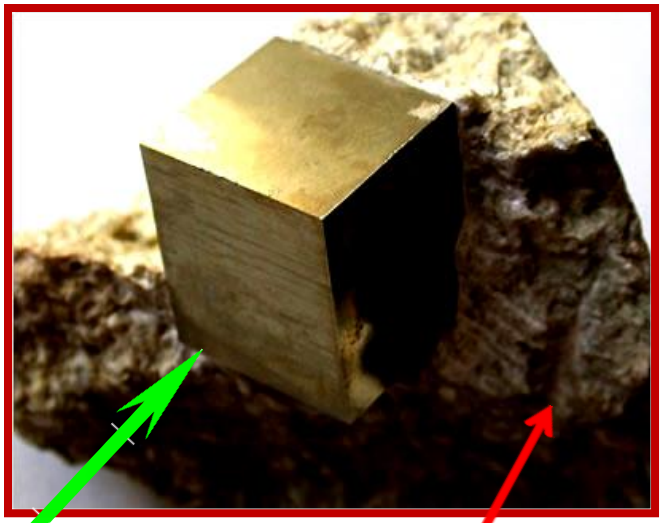
- ***Single Crystals***, ideally **have a high degree of order**, or regular geometric periodicity, throughout the ***entire volume of the material***.



- A ***Single Crystal*** has a arrangement of atoms that repeats periodically across its whole volume. Even at infinite length scales, each atom is related to each equivalent atom in the structure by translational symmetry.







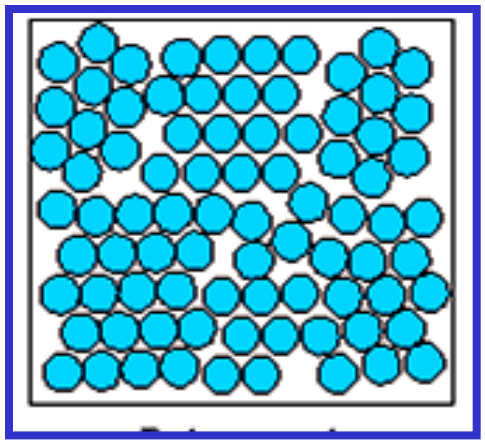
Single Crystals

Single Pyrite Crystal

Amorphous Solid

Polycrystalline Solids

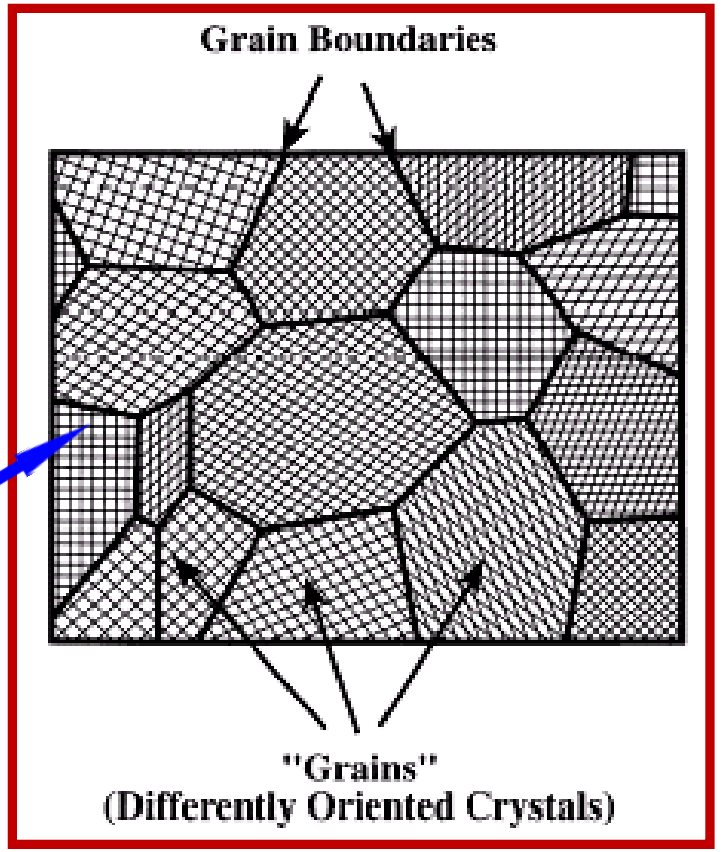
- A **Polycrystalline Solid** is made up of an aggregate of ***many small single crystals*** (crystallites or grains).
- Polycrystalline materials ***have a high degree of order over many atomic or molecular*** dimensions.
- These ***ordered regions*****,** or single crystal regions, **vary in size & orientation** with respect to one another.
- These regions are called ***grains (or domains)*** & are separated from one another by **grain boundaries.**



Polycrystalline Pyrite Grain

Polycrystalline Solids

- In **Polycrystalline Solids**, the **atomic order** can vary from **one domain to the next.** The grains are usually ***100 nm - 100 microns in diameter***. Polycrystals with grains that are **< 10 nm** in diameter are called **nanocrystallites**.



A polycrystal with grain boundaries

Polycrystalline Solids

- Polycrystalline solids

with grains & grain boundaries:

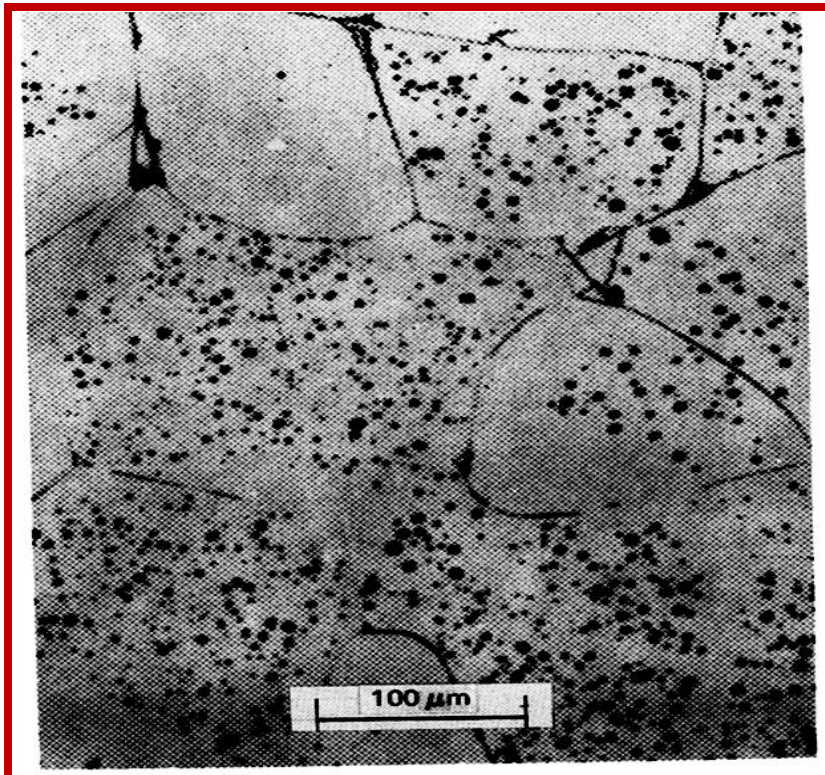


FIGURE 12.11 Microstructure of sintered Al_2O_3 showing the absence of porosity adjacent to grain boundaries and residual porosity within the grains. (Courtesy of J. E. Burke, General Electric Co.)

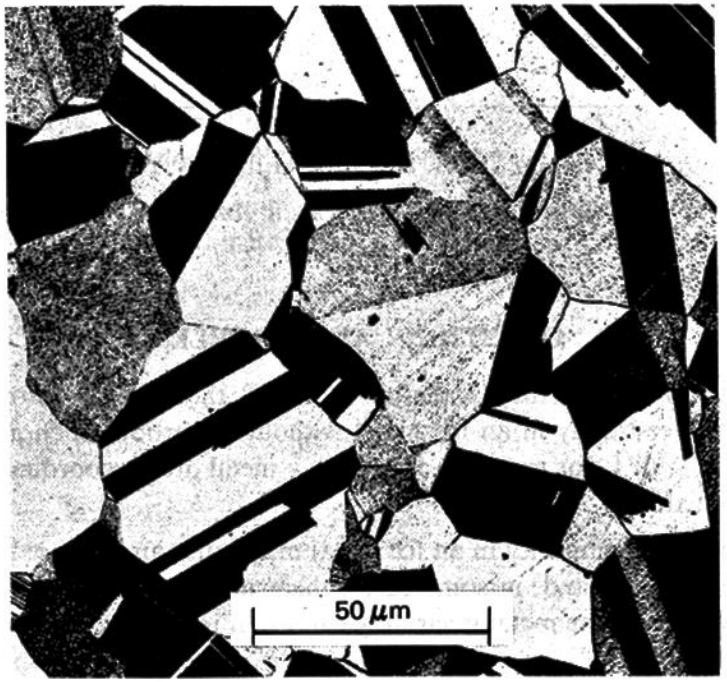
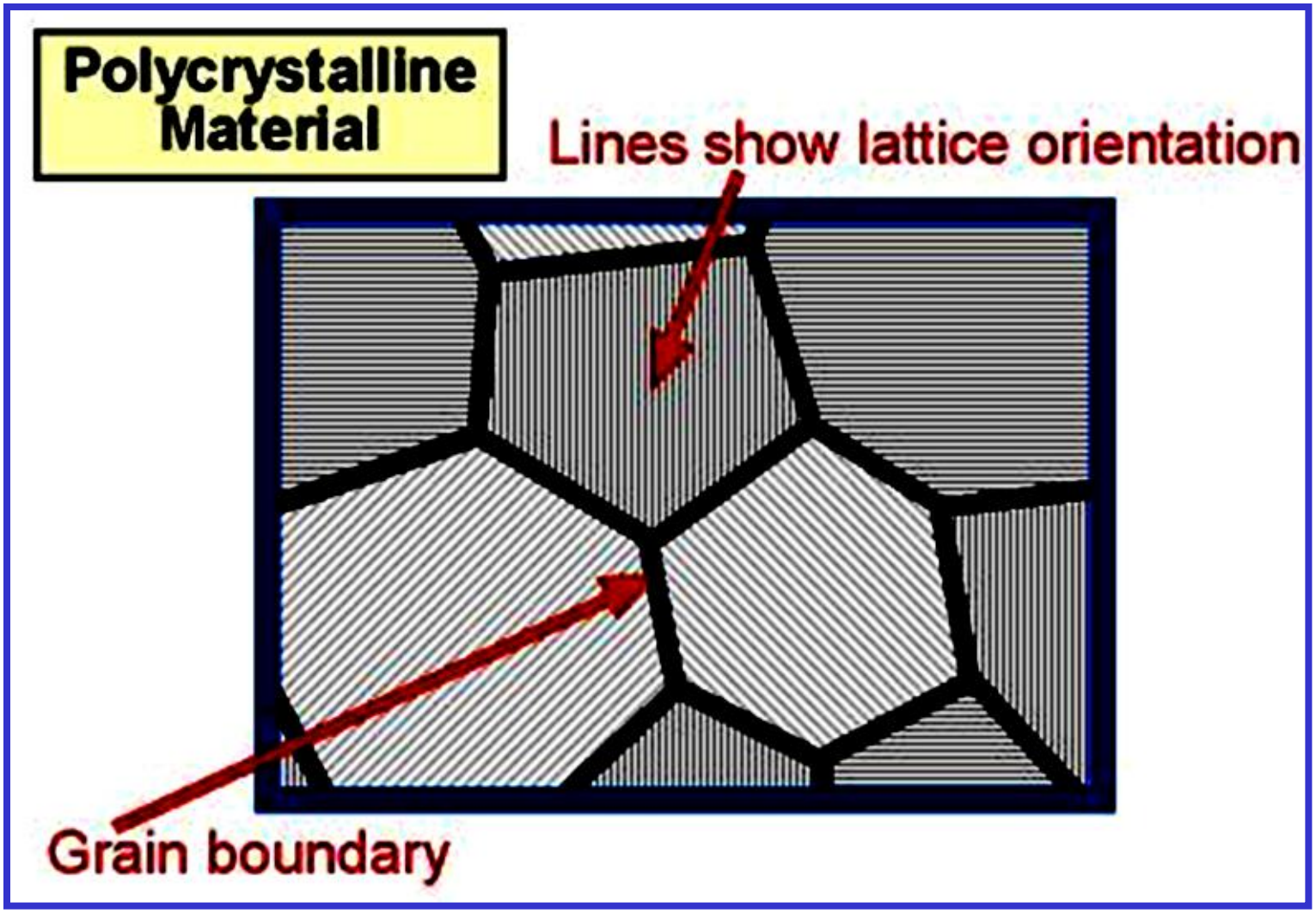
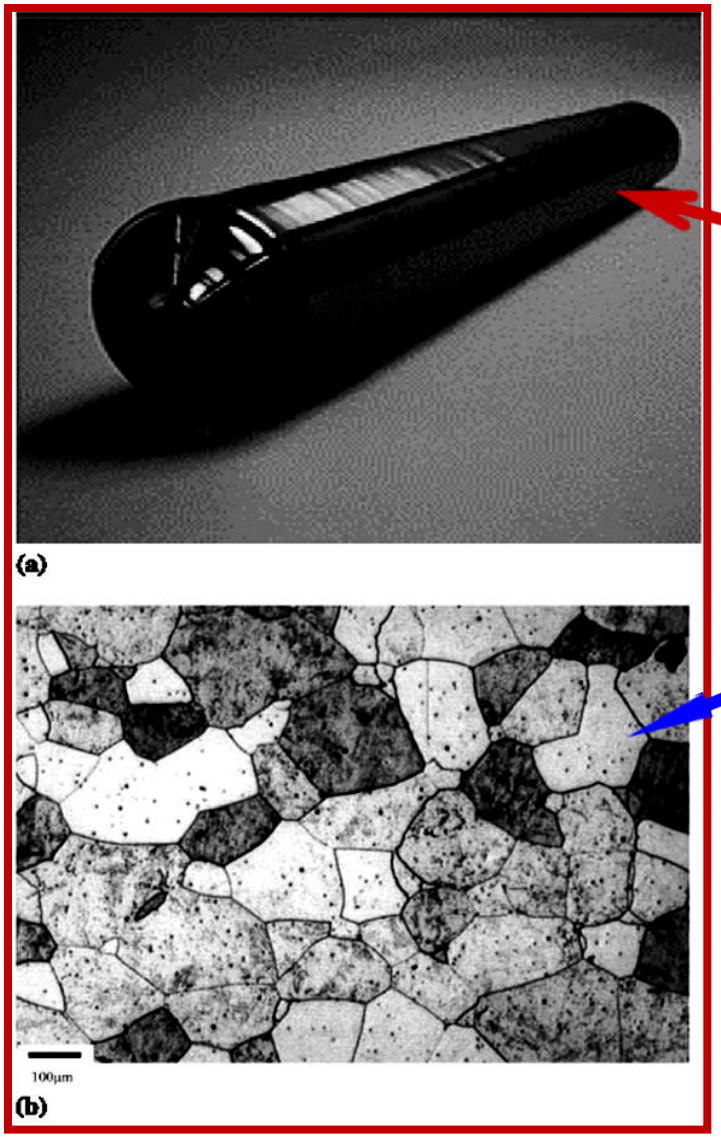


FIGURE 10.18 The microstructure of annealed cartridge brass (70% Cu–30% Zn). Within many grains, twins (the regions with parallel sides) and twin boundaries are apparent. The contrast between twinned regions of an individual grain is a result of differing attack by the chemical etchant acting on different orientations.

Polycrystalline Solids



Polycrystalline Solids



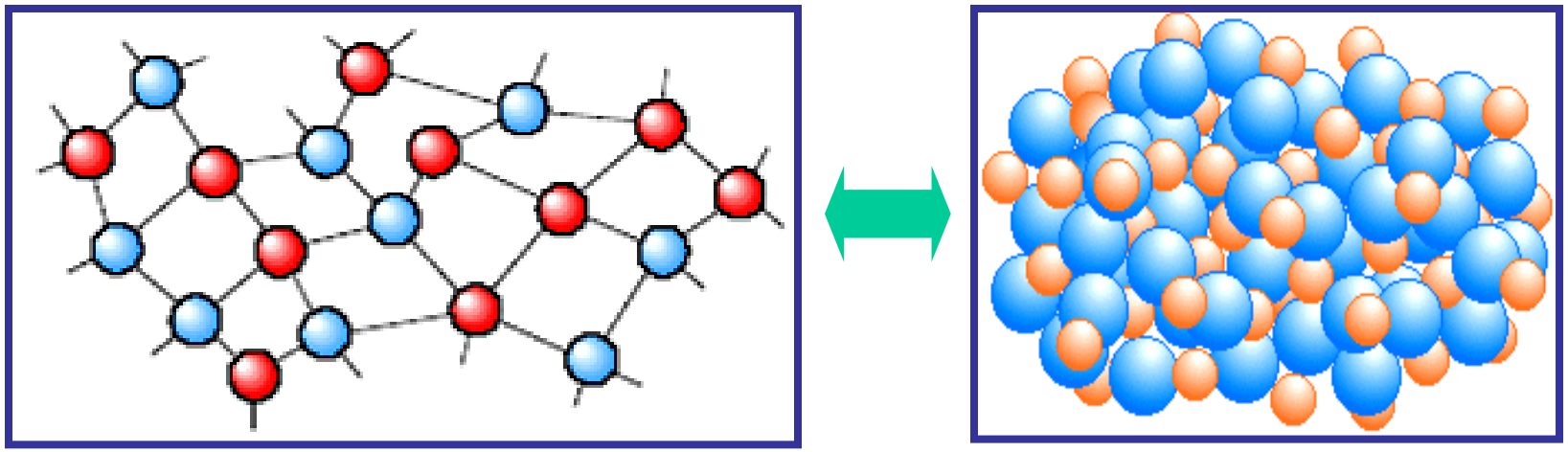
Photograph of a Silicon Single Crystal.

Micrograph of a Polycrystalline stainless steel sample showing grains & grain boundaries

Amorphous Solids

Amorphous (Non-Crystalline) Solids

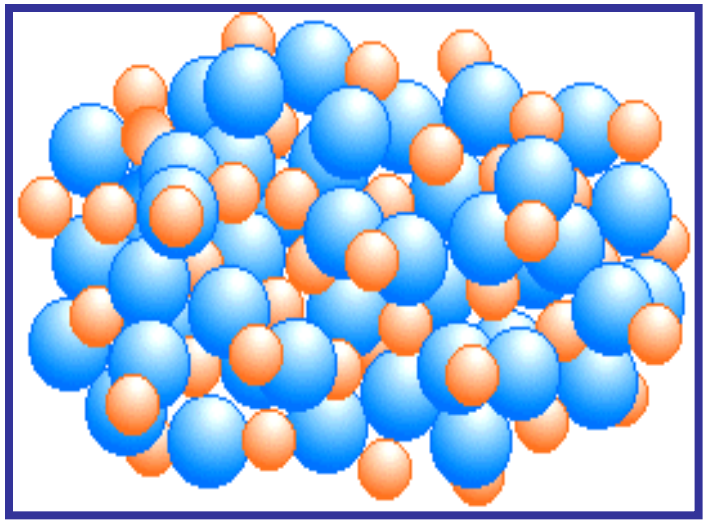
- Are composed of randomly oriented atoms, ions, or molecules that do not form defined patterns or lattice structures.
- Amorphous materials have order only within a few atomic or molecular dimensions.



Amorphous Solids

Amorphous (Non-crystalline) Solids

- Have order only within a few atomic or molecular dimensions. They do not have any long-range order, but they have varying degrees of short-range order. Examples of amorphous materials include amorphous silicon, plastics, & glasses.



Amorphous Solids

Amorphous (Non-crystalline) Solids

- Have no regular, long range order of arrangement of atoms.

Some examples from everyday life:

1. Polymers, 2. Ceramics,

3. Window Glass

- The two sub-states of amorphous solids are the **Rubbery and Glassy states**

Amorphous Solids

- Have no regular, long range order of arrangement of atoms.
- Can be prepared by rapidly cooling molten material. Rapid cooling minimizes time for the atoms to pack into a more thermodynamically favorable crystalline state.

Amorphous Solids

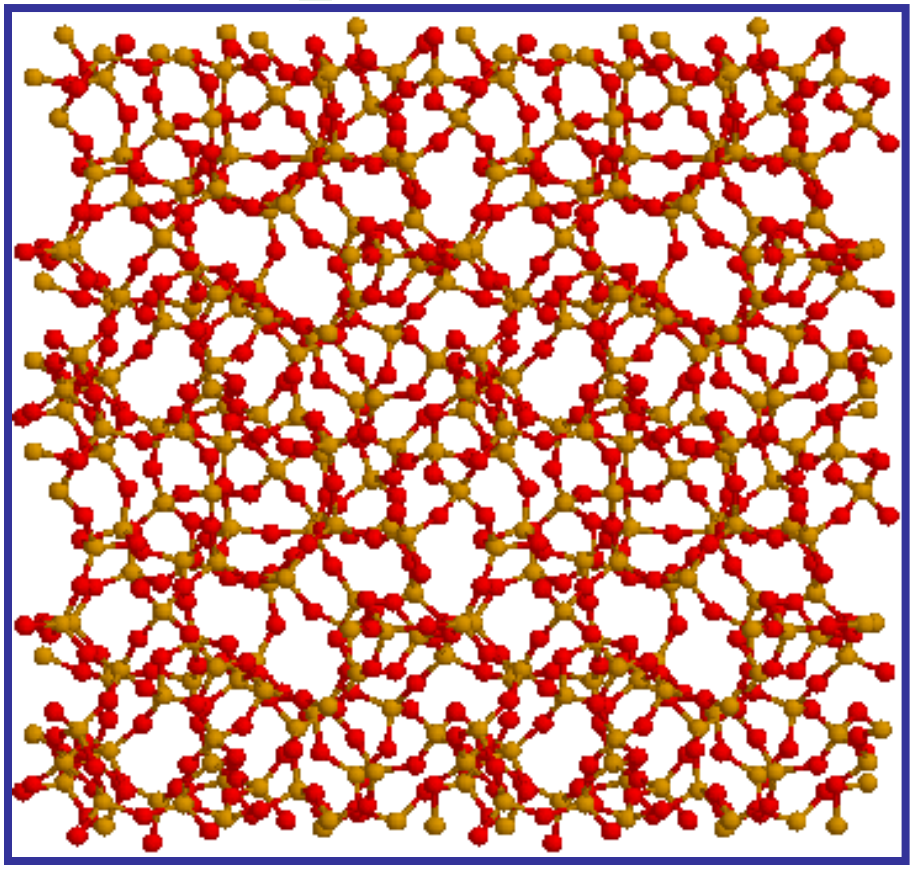


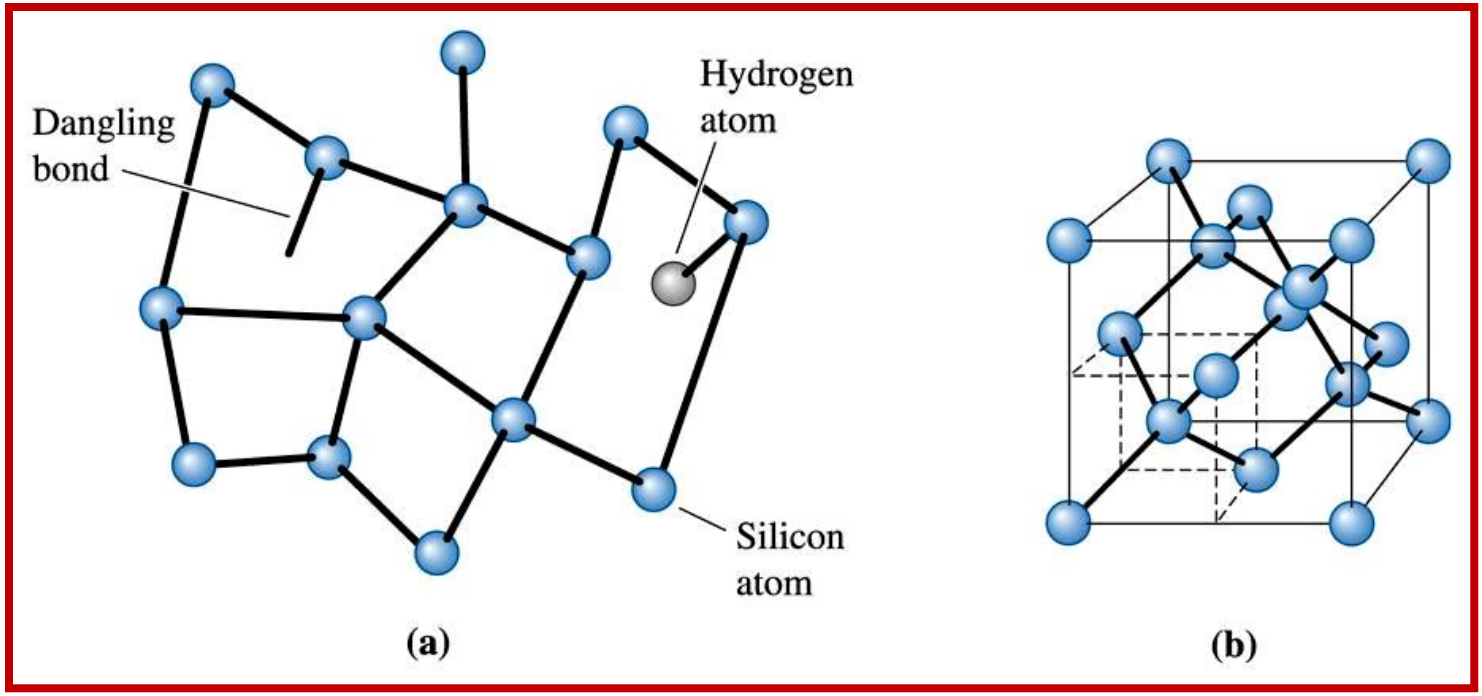
Illustration of the continuous random network structure of the atoms in an amorphous solid

Amorphous Solids

- **Amorphous Materials** ≡ Materials, including glasses, that have no long-range order, or crystal structure.

- **Glasses** - Solid, non-crystalline materials (typically derived from the molten state) that have only short-range atomic order.

- **Glass-Ceramics** - A family of materials typically derived from molten inorganic glasses & processed into crystalline materials with very fine grain size & improved mechanical properties.



- Atomic arrangements in crystalline silicon & amorphous silicon.

(a) Amorphous silicon **(b) Crystalline silicon**

- Note the variation in the inter-atomic distance for amorphous silicon.

Crystals

- The periodic array of atoms, ions, or molecules that form the solid is called the ***Crystal Structure***

Crystal Structure ≡

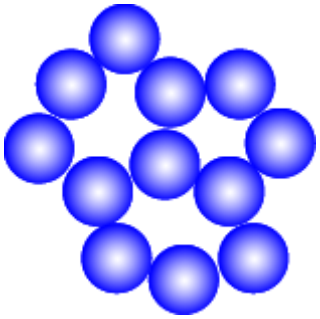
Space **(Crystal)** ***Lattice*** **+** ***Basis***

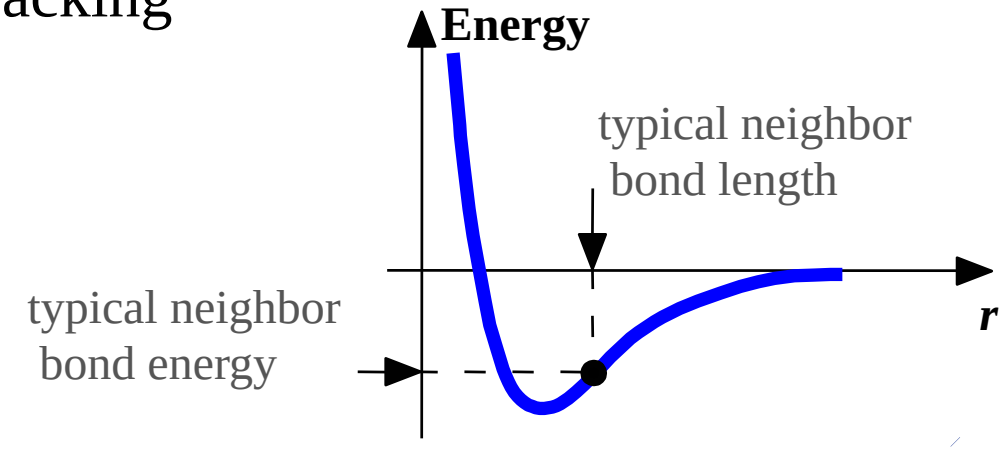
- **The Space (Crystal) Lattice** is a regular periodic arrangement of ***POINTS*** in space, ***& is purely a mathematical abstraction.***
- A **Crystal Structure** is formed by "putting" the identical atoms (or group of atoms) on the points of the space lattice

This group of atoms is called the ***Basis***

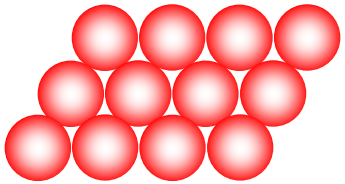
Energy and Packing

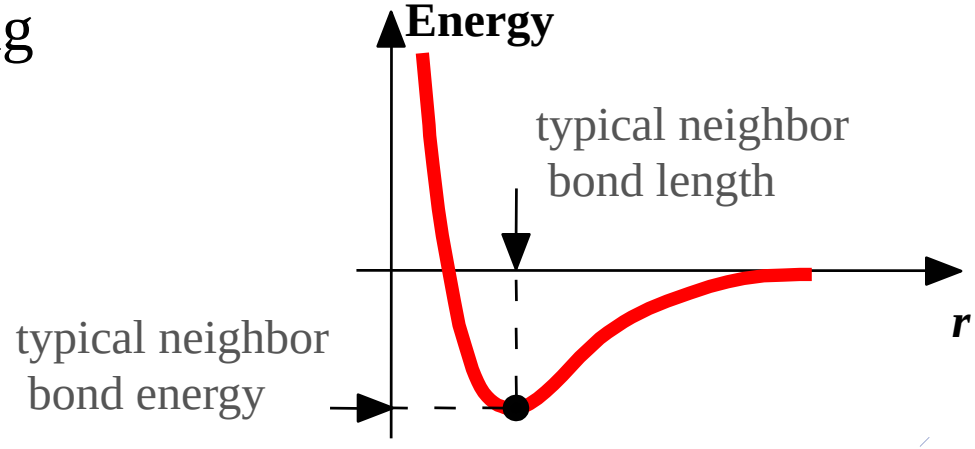
- Non dense, random packing





- Dense, ordered packing



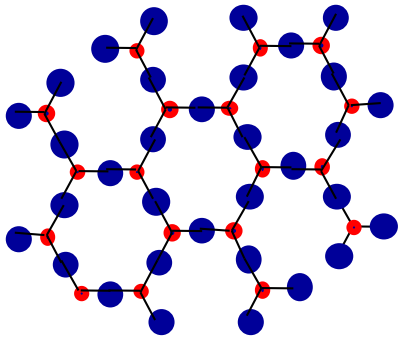


Dense, ordered packed structures tend to have lower energies.

Materials and Packing

Crystalline materials...

- atoms pack in periodic, 3D arrays
- typical of: -metals
  -many ceramics
  -some polymers



crystalline SiO_2

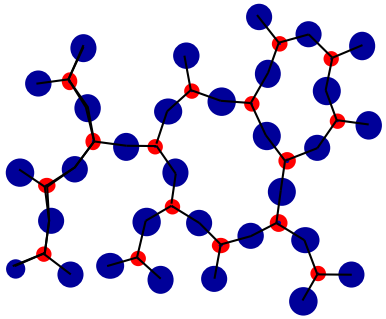
Adapted from Fig. 3.23(a), *Callister & Rethwisch 8e.*

• **Si** ● **Oxygen**

Noncrystalline materials...

- atoms have no periodic packing
- occurs for: -complex structures
  -rapid cooling

"Amorphous" = Noncrystalline



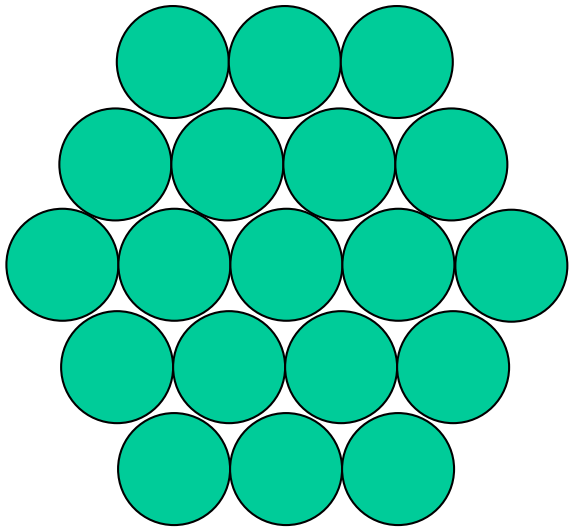
noncrystalline SiO_2

Adapted from Fig. 3.23(b), *Callister & Rethwisch 8e.*

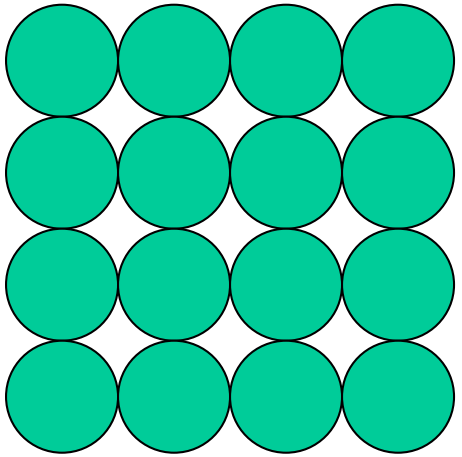
Metallic Crystal Structures

- How can we stack metal atoms to minimize empty space?

2-dimensions



vs.

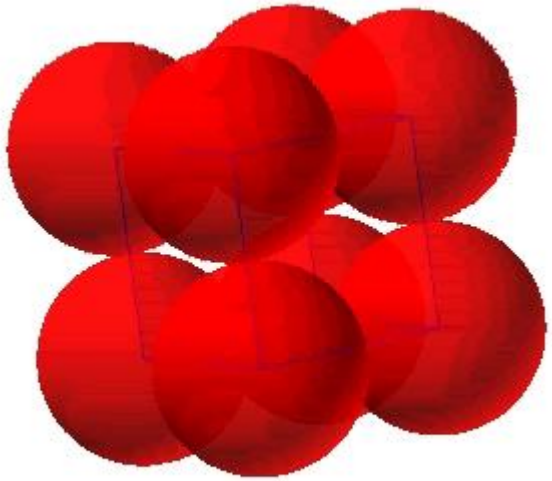


Metallic Crystal Structures

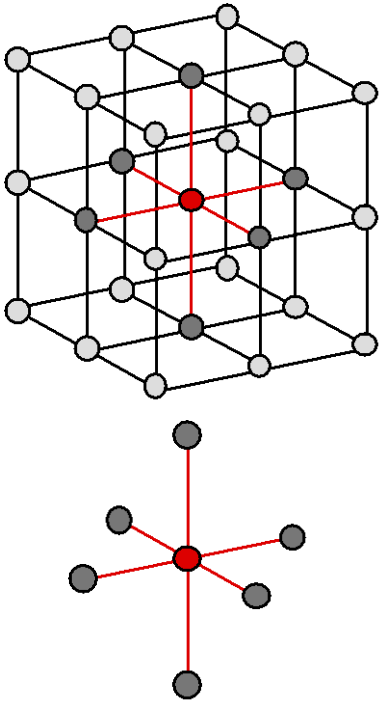
- Tend to be densely packed.
- Reasons for dense packing:
  - Typically, only one element is present, so all atomic radii are the same.
  - Metallic bonding is not directional.
  - Nearest neighbor distances tend to be small in order to lower bond energy.
  - Electron cloud shields cores from each other
- Have the simplest crystal structures.

Simple Cubic Structure (SC)

- Rare due to low packing density (only Po has this structure)
- Close-packed directions are cube edges.



- Coordination # = 6
  (# nearest neighbors)

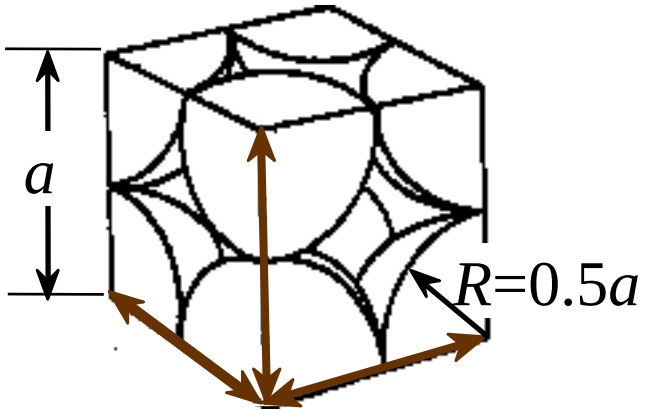


Atomic Packing Factor (APF)

$$APF = \frac{\text{Volume of atoms in unit cell*}}{\text{Volume of unit cell}}$$

*assume hard spheres

- APF for a simple cubic structure = 0.52



close-packed directions

contains 8 x 1/8 =
1 atom/unit cell

$$APF = \frac{\text{atoms}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}} \Big/ \frac{\text{volume}}{\text{unit cell}}$$

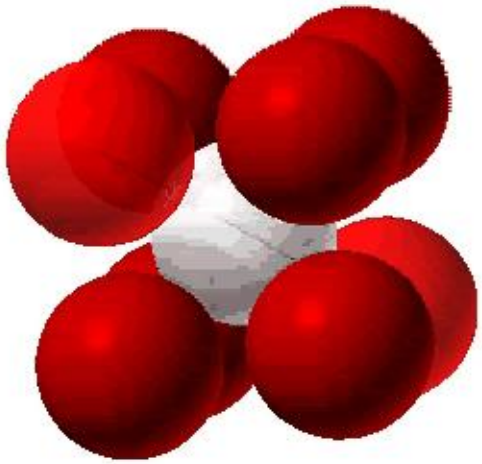
$$APF = \frac{1 \cdot \frac{4}{3}\pi (0.5a)^3}{a^3}$$

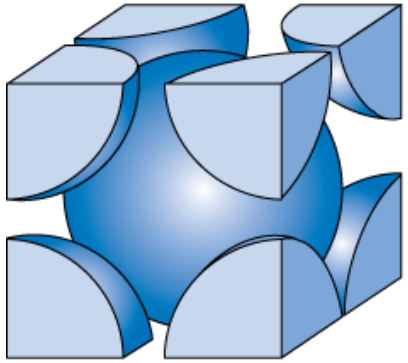
Body Centered Cubic Structure (BCC)

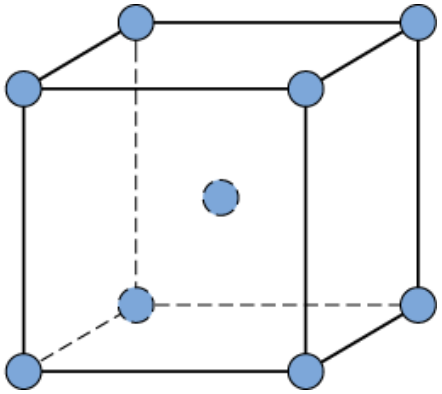
- Atoms touch each other along cube diagonals.
  --Note: All atoms are identical; the center atom is shaded differently only for ease of viewing.

ex: Cr, W, Fe (α), Tantalum, Molybdenum

- Coordination # = 8





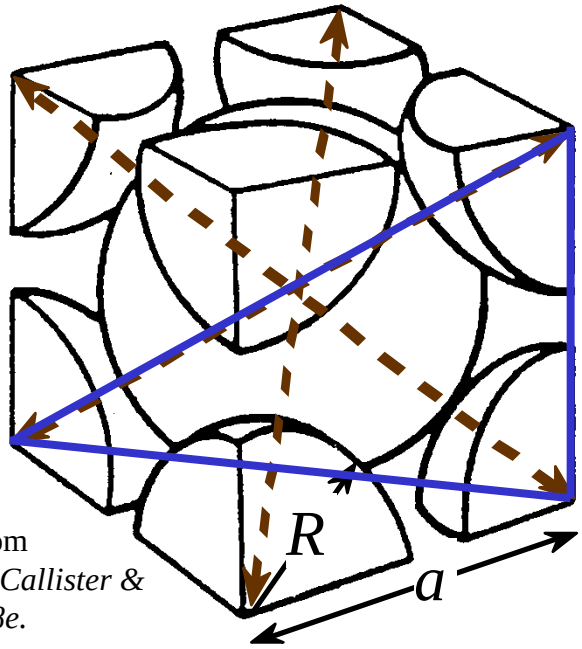


Adapted from Fig. 3.2,
Callister & Rethwisch 8e.

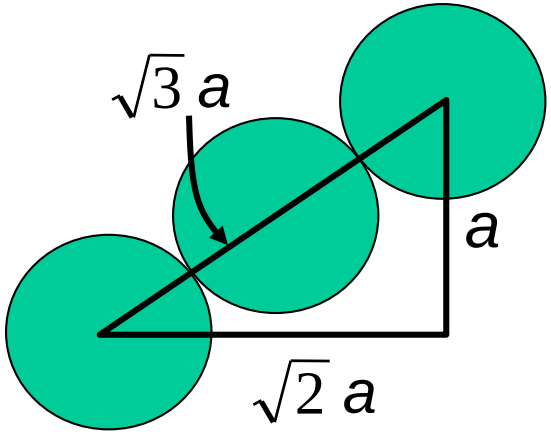
2 atoms/unit cell: 1 center + 8 corners x 1/8

Atomic Packing Factor: BCC

- APF for a body-centered cubic structure = 0.68



Adapted from Fig. 3.2(a), *Callister & Rethwisch 8e.*



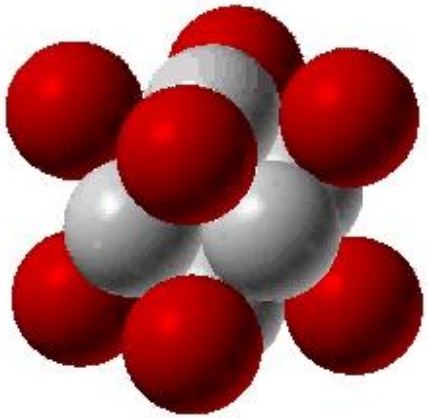
$$APF = \frac{\text{atoms}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}} \Big/ \frac{\text{volume}}{\text{unit cell}} = \frac{2 \cdot \frac{4}{3}\pi (\sqrt{3}a/4)^3}{a^3}$$

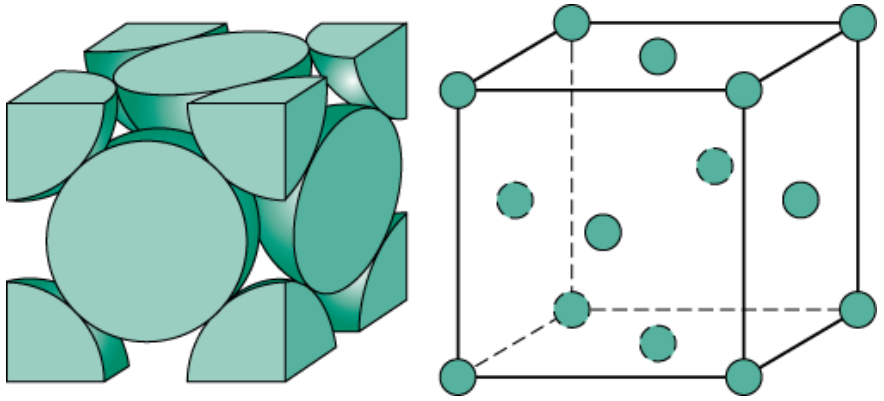
Face Centered Cubic Structure (FCC)

- Atoms touch each other along face diagonals.
  --Note: All atoms are identical; the face-centered atoms are shaded differently only for ease of viewing.

ex: Al, Cu, Au, Pb, Ni, Pt, Ag

- Coordination # = 12





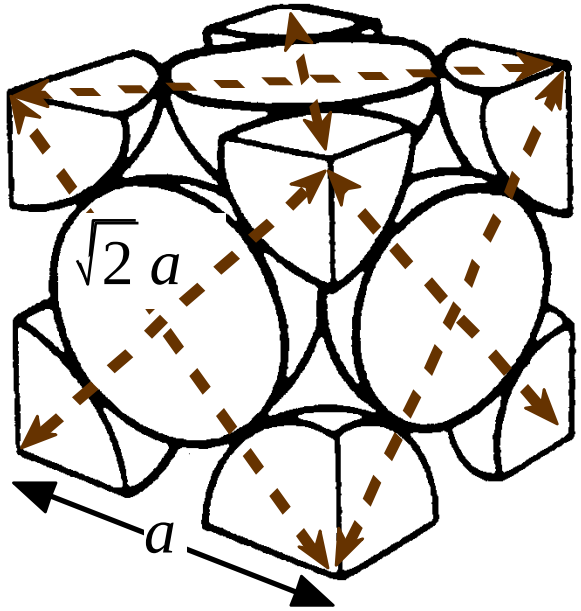
Adapted from Fig. 3.1, *Callister & Rethwisch 8e.*

4 atoms/unit cell: 6 face x 1/2 + 8 corners x 1/8

Atomic Packing Factor: FCC

- APF for a face-centered cubic structure = 0.74

maximum achievable APF



Unit cell contains:

6 x 1/2 + 8 x 1/8

= 4 atoms/unit cell

$$APF = \frac{\dfrac{\text{atoms}}{\text{unit cell}} \leftarrow 4 \quad \dfrac{4}{3}\pi\left(\dfrac{\sqrt{2}a}{4}\right)^3 \rightarrow \dfrac{\text{volume}}{\text{atom}}}{a^3 \leftarrow \dfrac{\text{volume}}{\text{unit cell}}}$$

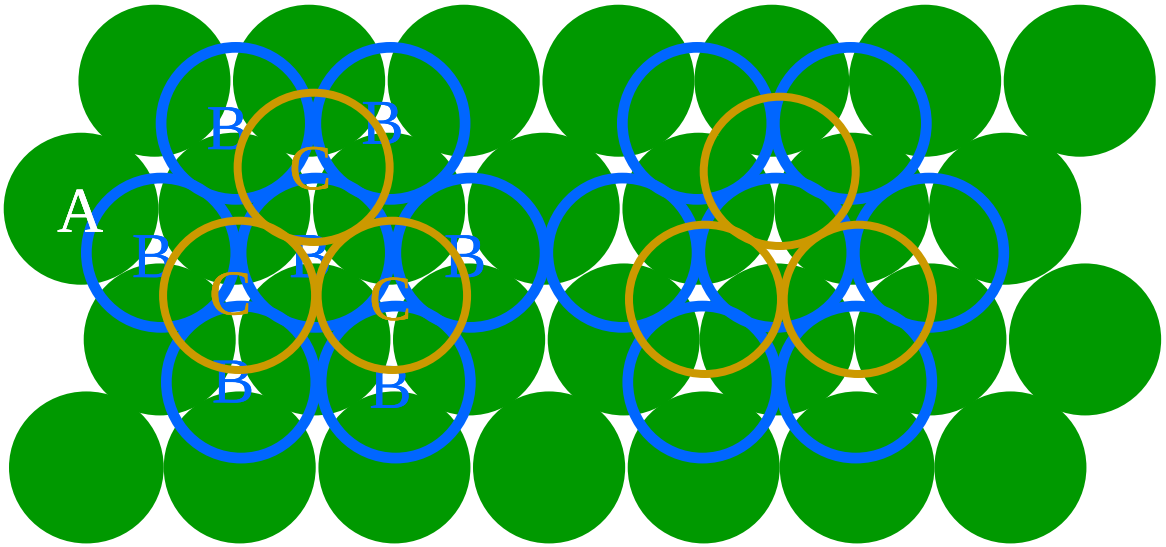
FCC Stacking Sequence

- ABCABC... Stacking Sequence
- 2D Projection

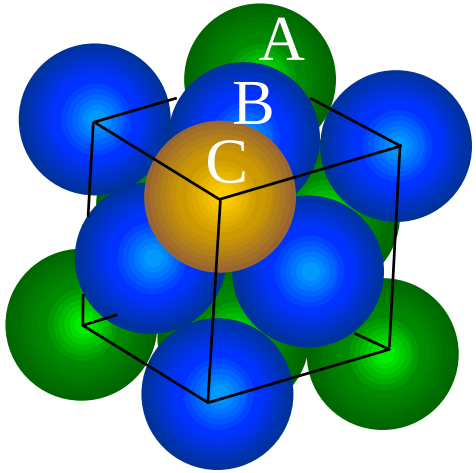
A sites

B sites

C sites

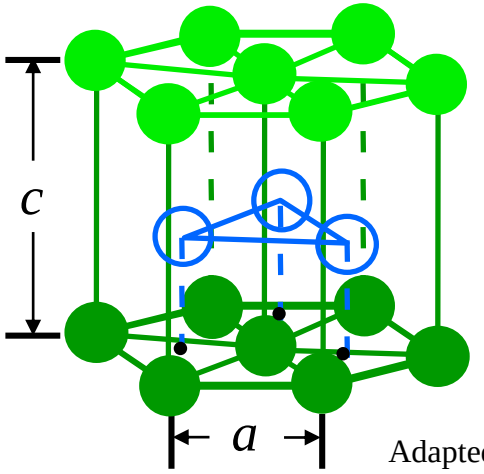


- FCC Unit Cell



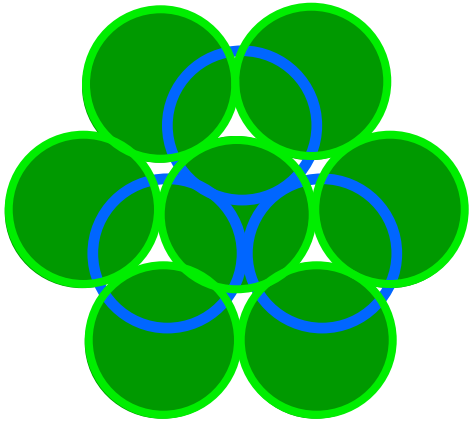
Hexagonal Close-Packed Structure (HCP)

- ABAB... Stacking Sequence
- 3D Projection



Adapted from Fig. 3.3(a), *Callister & Rethwisch 8e.*

- 2D Projection



- Coordination # = 12
- APF = 0.74

6 atoms/unit cell

ex: Cd, Mg, Ti, Zn

Theoretical Density, ρ

$$\text{Density} = \rho = \frac{\text{Mass of Atoms in Unit Cell}}{\text{Total Volume of Unit Cell}}$$

$$\rho = \frac{n A}{V_C N_A}$$

where n = number of atoms/unit cell

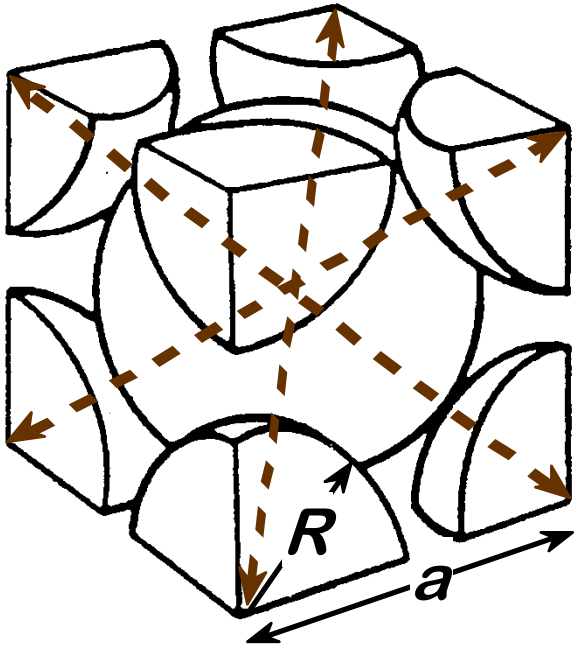
A = atomic weight

V_C = Volume of unit cell = a^3 for cubic

N_A = Avogadro's number

= 6.022×10^{23} atoms/mol

Theoretical Density, ρ



- Ex: Cr (BCC)

  A = 52.00 g/mol

  R = 0.125 nm

  n = 2 atoms/unit cell

$a = 4R/\sqrt{3} = 0.2887$ nm

$$\rho = \frac{\dfrac{\text{atoms}}{\text{unit cell}} \times \dfrac{\text{g}}{\text{mol}}}{\text{volume} \times \dfrac{\text{atoms}}{\text{mol}}} = \frac{2 \times 52.00}{a^3 \times 6.022 \times 10^{23}}$$

$\rho_{theoretical}$	= 7.18 g/cm^3
ρ_{actual}	= 7.19 g/cm^3

Densities of Material Classes

In general

$\rho_{metals} > \rho_{ceramics} > \rho_{polymers}$

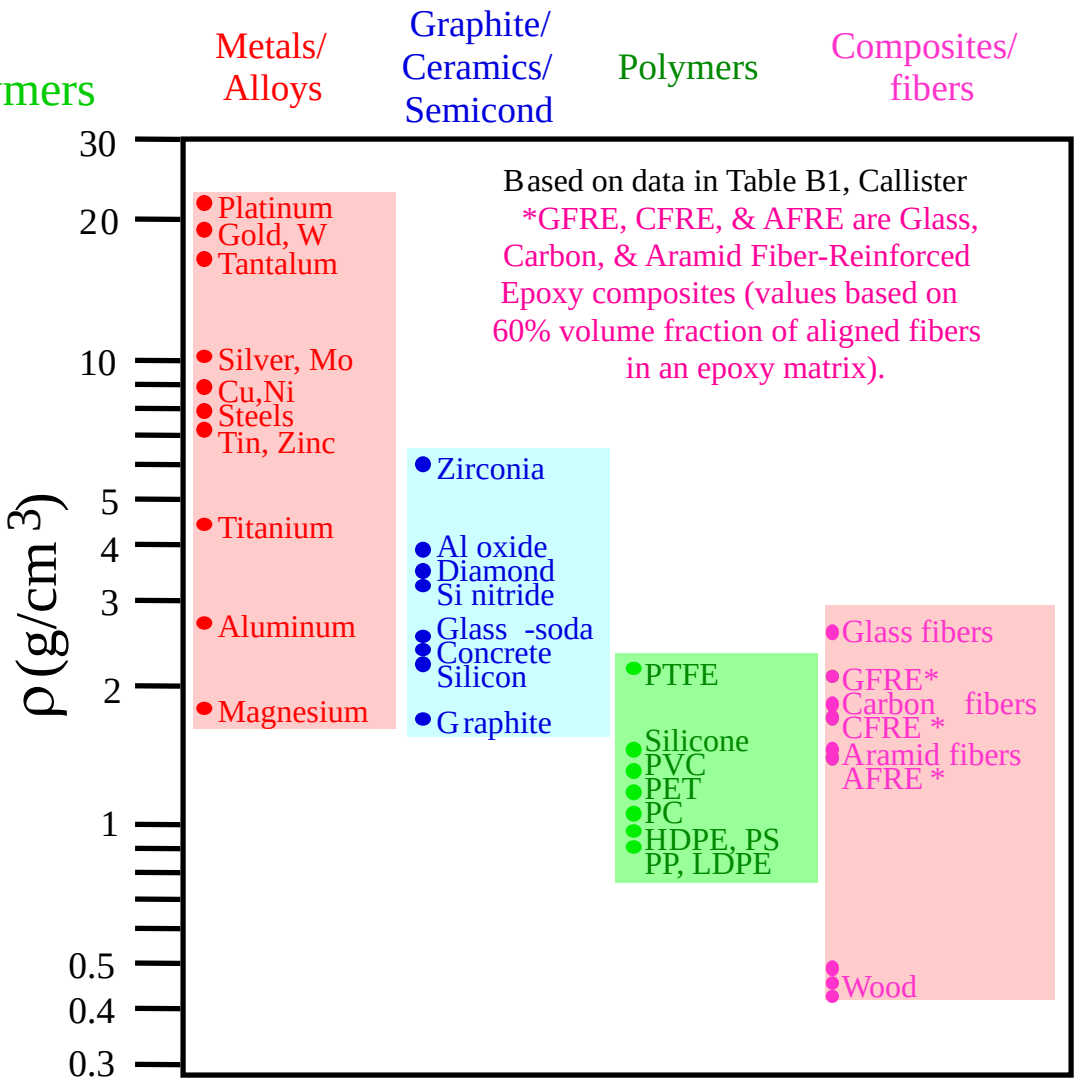
Why?

Metals have...
- close-packing (metallic bonding)
- often large atomic masses

Ceramics have...
- less dense packing
- often lighter elements

Polymers have...
- low packing density (often amorphous)
- lighter elements (C,H,O)

Composites have...
- intermediate values



Data from Table B.1, *Callister & Rethwisch, 8e.*

Crystals as Building Blocks

- *Some* engineering applications require single crystals:
  -- diamond single crystals for abrasives

  -- turbine blades

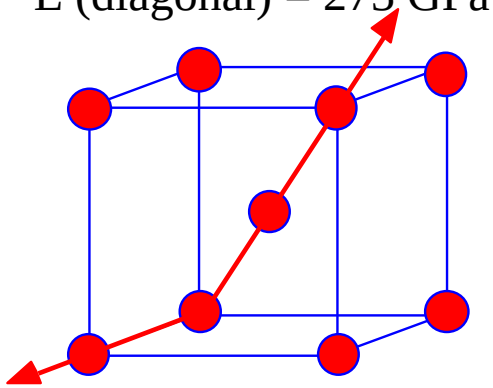
- Properties of crystalline materials often related to crystal structure.
  -- Ex: Quartz fractures more easily along some crystal planes than others.

(Courtesy P.M. Anderson)

Single vs Polycrystals

- Single Crystals
  - -Properties vary with direction: anisotropic.
  - -Example: the modulus of elasticity (E) in BCC iron:

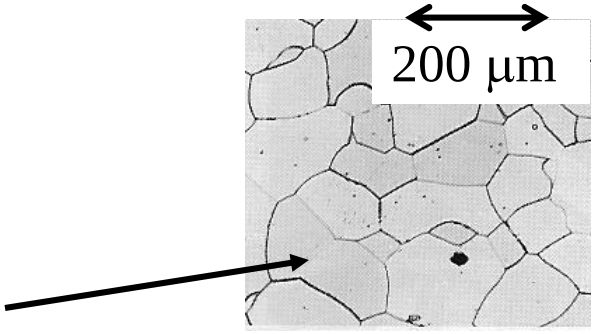
E (diagonal) = 273 GPa

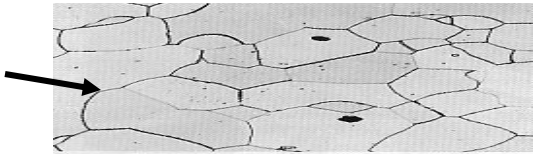


E (edge) = 125 GPa

Data from Table 3.3, *Callister & Rethwisch 8e*. (Source of data is R.W. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials*, 3rd ed., John Wiley and Sons, 1989.)

- Polycrystals
  - -Properties may/may not vary with direction.
  - -If grains are randomly oriented: isotropic. ($E_{poly\ iron}$ = 210 GPa)
  - -If grains are textured, anisotropic.



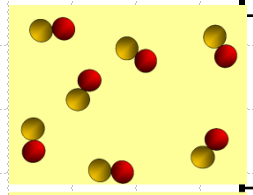
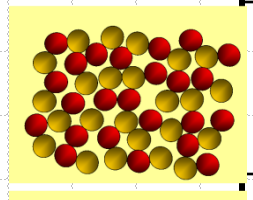
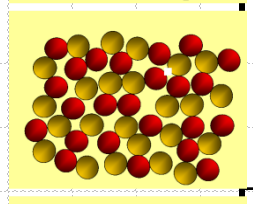
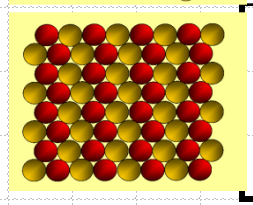


Adapted from Fig. 4.14(b), *Callister & Rethwisch 8e*. (Fig. 4.14(b) is courtesy of L.C. Smith and C. Brady, the National Bureau of Standards, Washington, DC [now the National Institute of Standards and Technology, Gaithersburg, MD].)

Geometry of Crystals

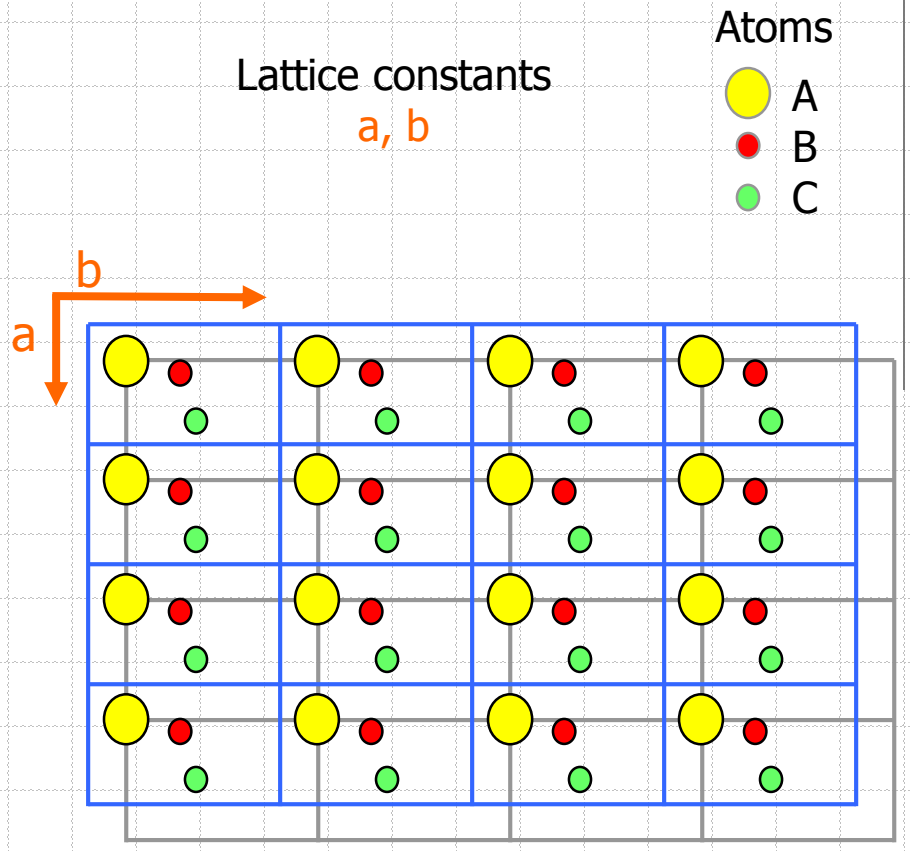
Crystal is a solid composed of atoms, ions or molecules that demonstrate long range periodic order in three dimensions

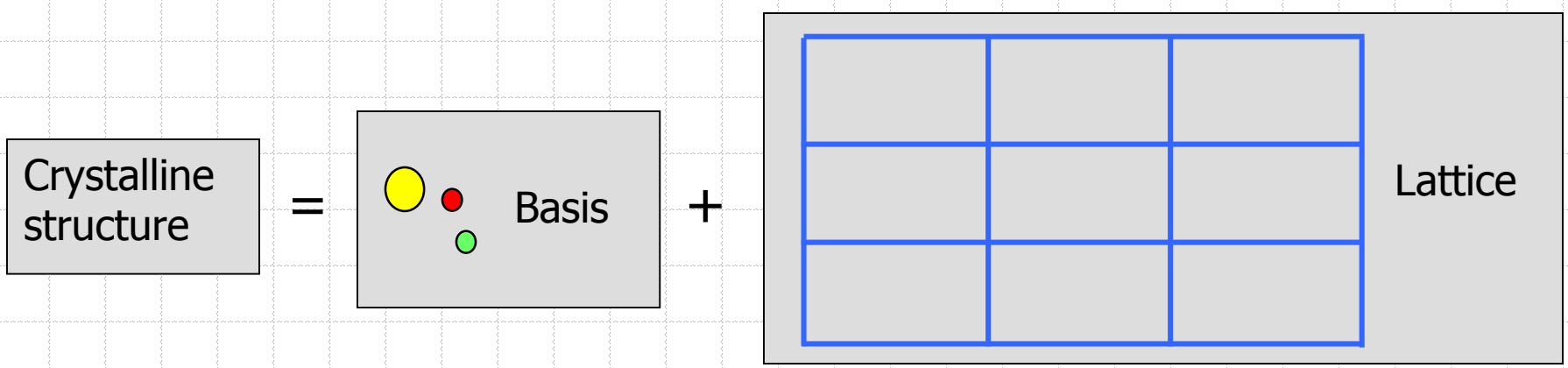
The Crystalline State

	State of Matter	Fixed Volume	Fixed Shape	Order	Properties
	Gas	No	No	No	Isotropic
	Liquid	Yes	No	Short-range	Isotropic
	Solid (amorphous)	Yes	Yes	Short-range	Isotropic
	Solid (crystalline)	Yes	Yes	Long-range	Anisotropic

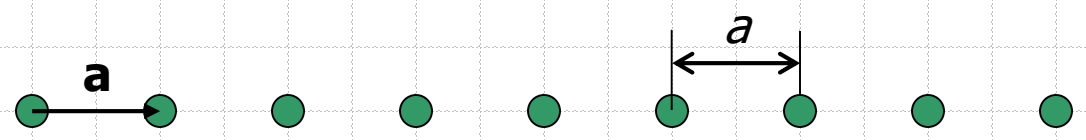
Crystal Lattice

- Not only atom, ion or molecule positions are repetitious – there are certain symmetry relationships in their arrangement.



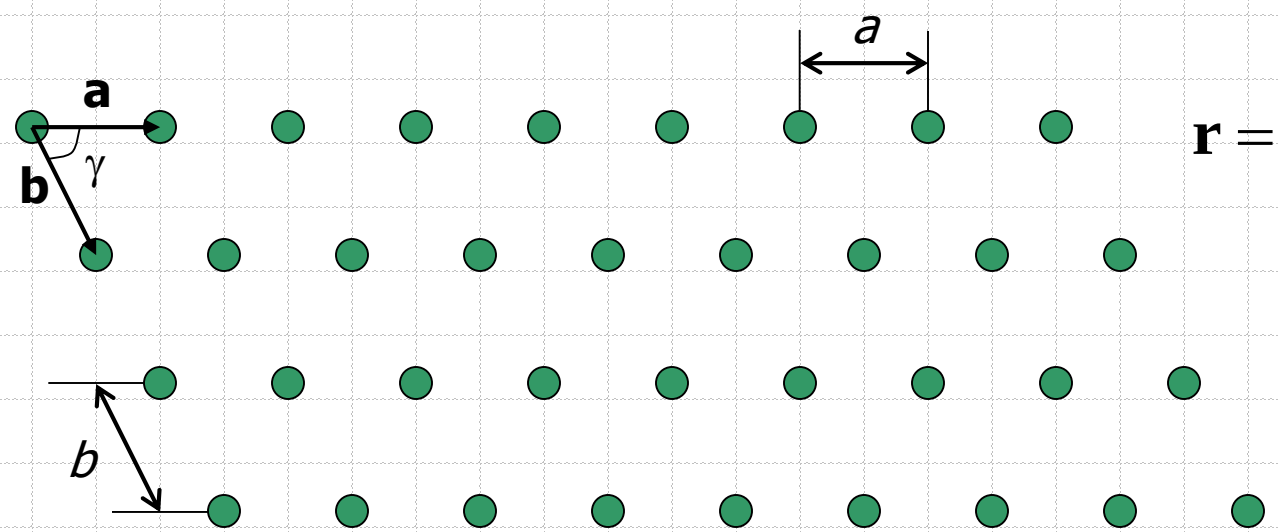


Crystal Lattice



$$\mathbf{r} = u\mathbf{a}$$

One-dimensional lattice with lattice parameter *a*

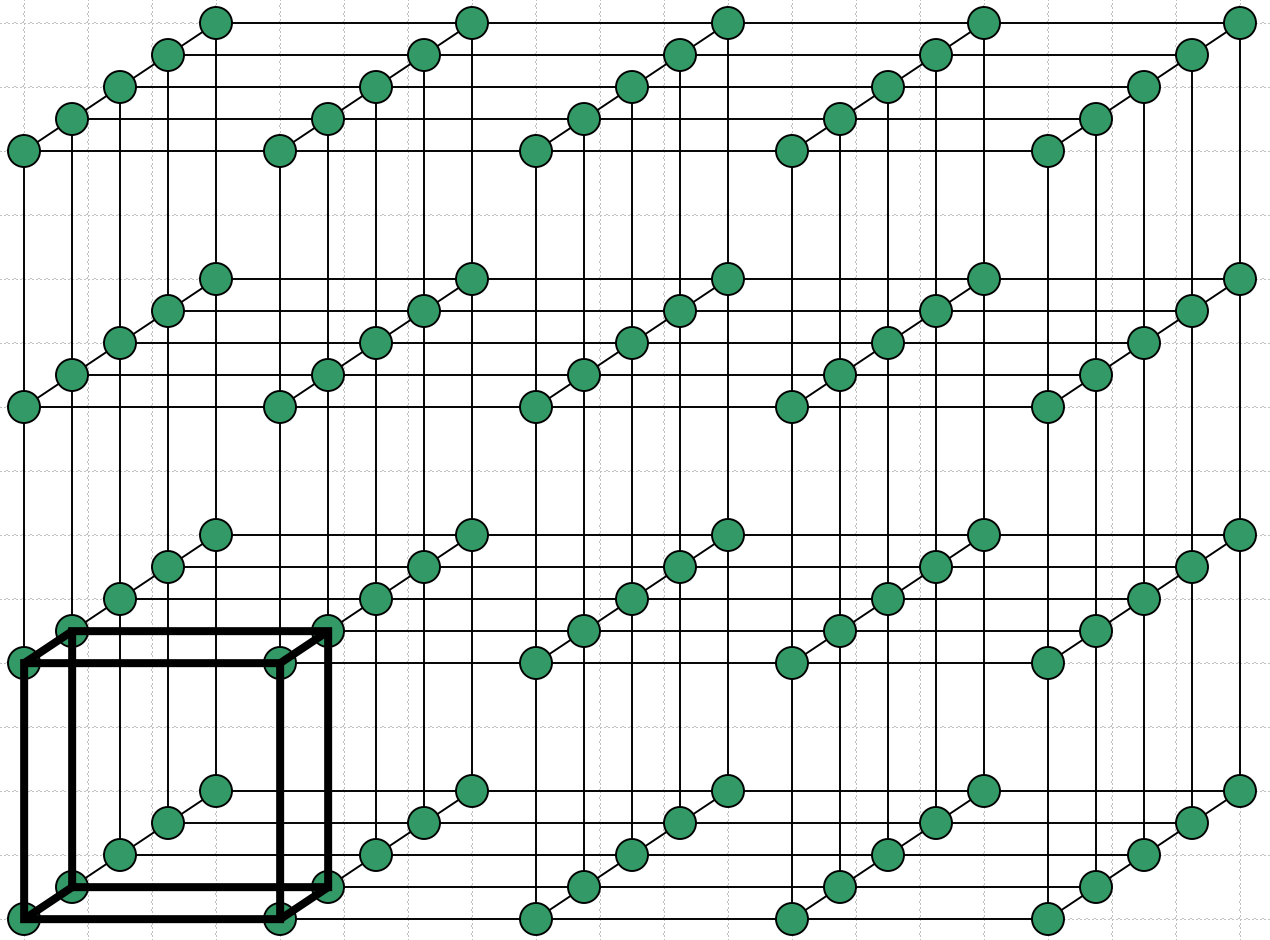


$$\mathbf{r} = u\mathbf{a} + v\mathbf{b}$$

Two-dimensional lattice with lattice parameters *a*, *b* and γ

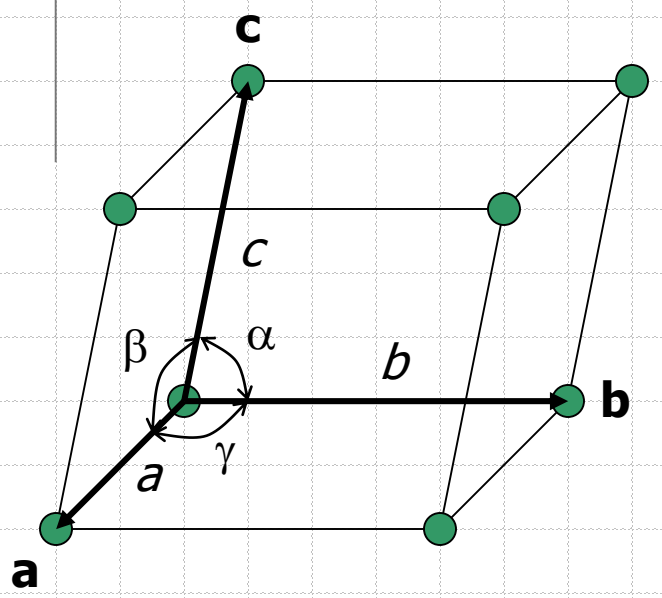
Crystal Lattice

$$\mathbf{r} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$$



Crystal Lattice

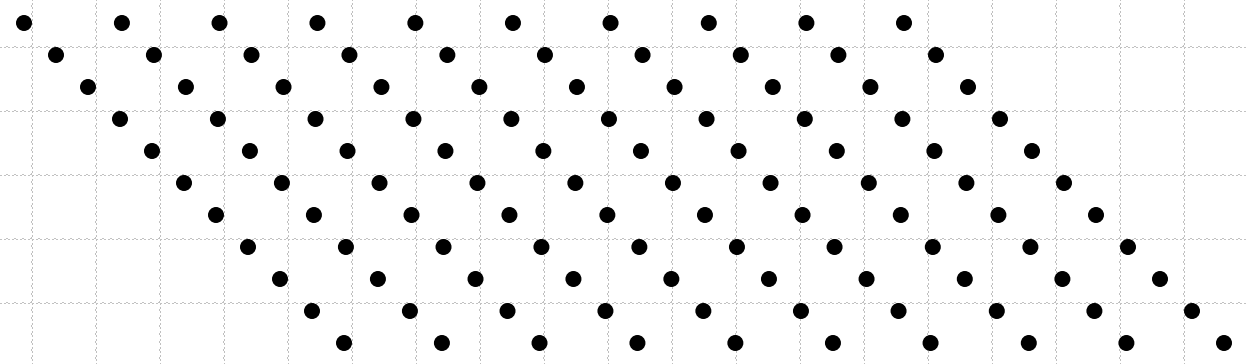
- Lattice vectors, lattice parameters and interaxial angles



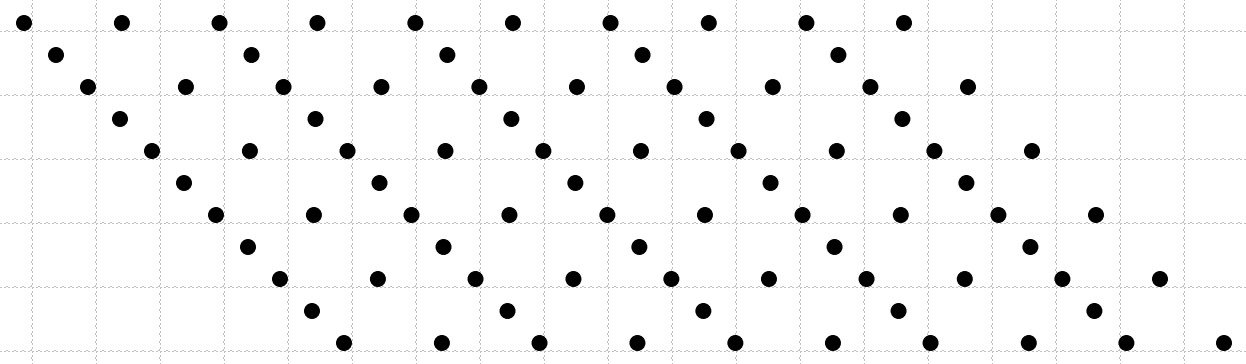
Lattice vector	**a**	**b**	**c**
Lattice parameter	*a*	*b*	*c*
Interaxial angle	α	β	γ

A lattice is an array of points in space in which the environment of each point is identical

Crystal Lattice



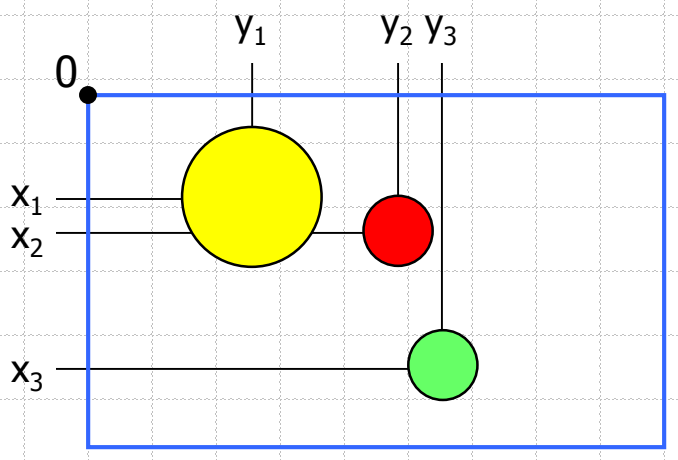
Lattice



Not a lattice

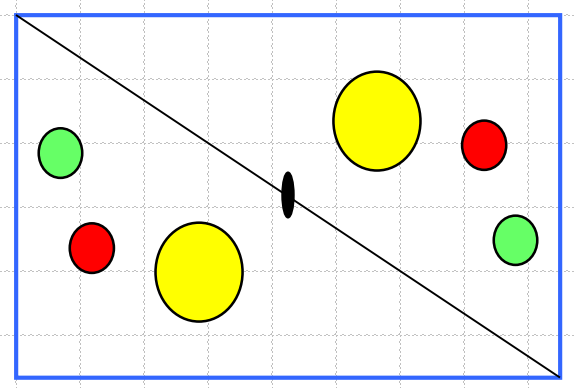
Crystal Lattice

- Unit cell content
  - Coordinates of all atoms
  - Types of atoms
  - Site occupancy
  - Individual displacement parameters

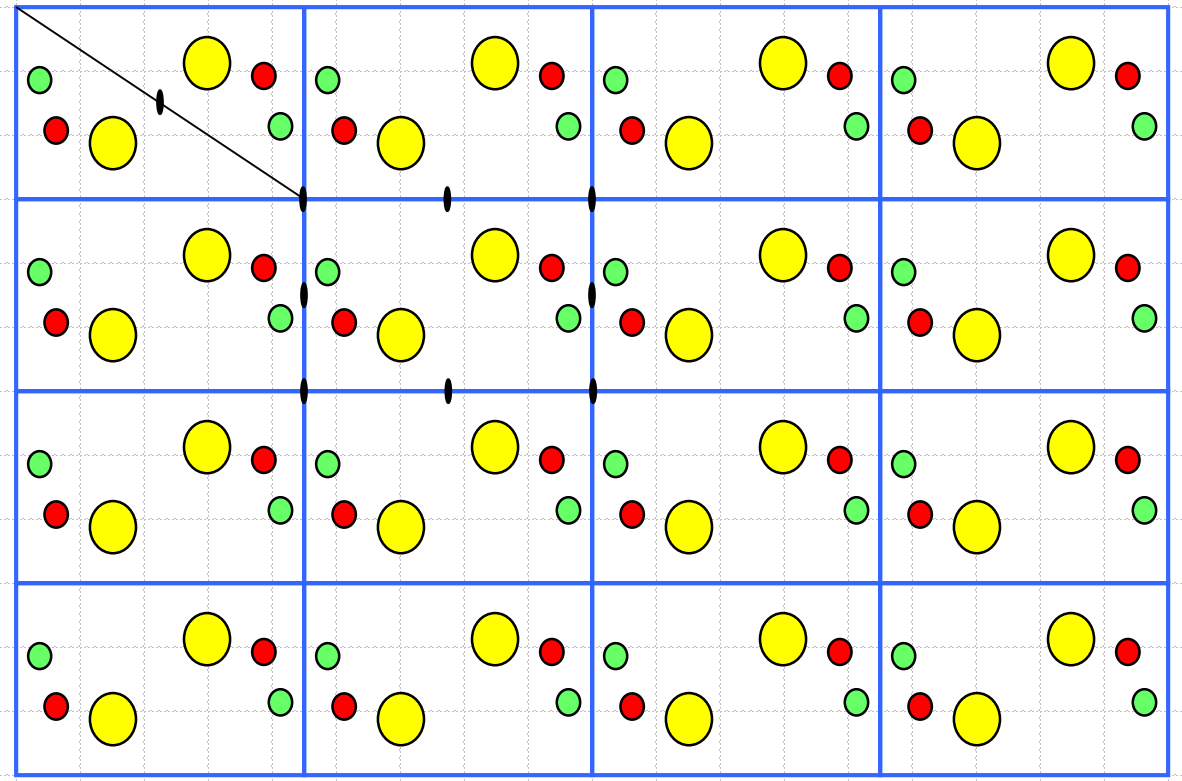


Crystal Lattice

- Usually unit cell has more than one molecule or group of atoms
- They can be represented by symmetry operators



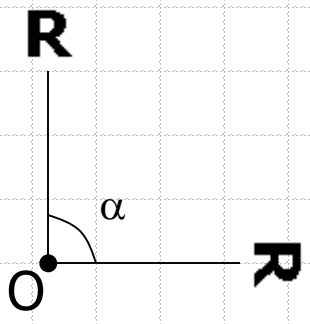
rotation



Symmetry

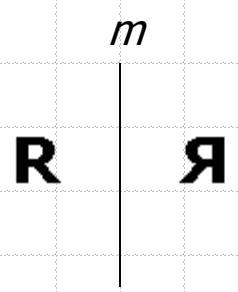
- Symmetry is a property of a crystal which is used to describe repetitions of a pattern within that crystal.
- Description is done using symmetry operators

Translation

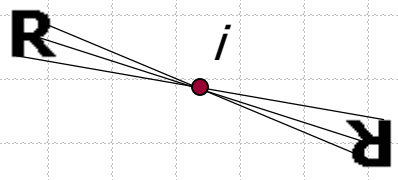


Rotation (about axis O)

$\alpha = 360°/n$
where n is the *fold* of the axis
n = 1, 2, 3, 4 or 6)



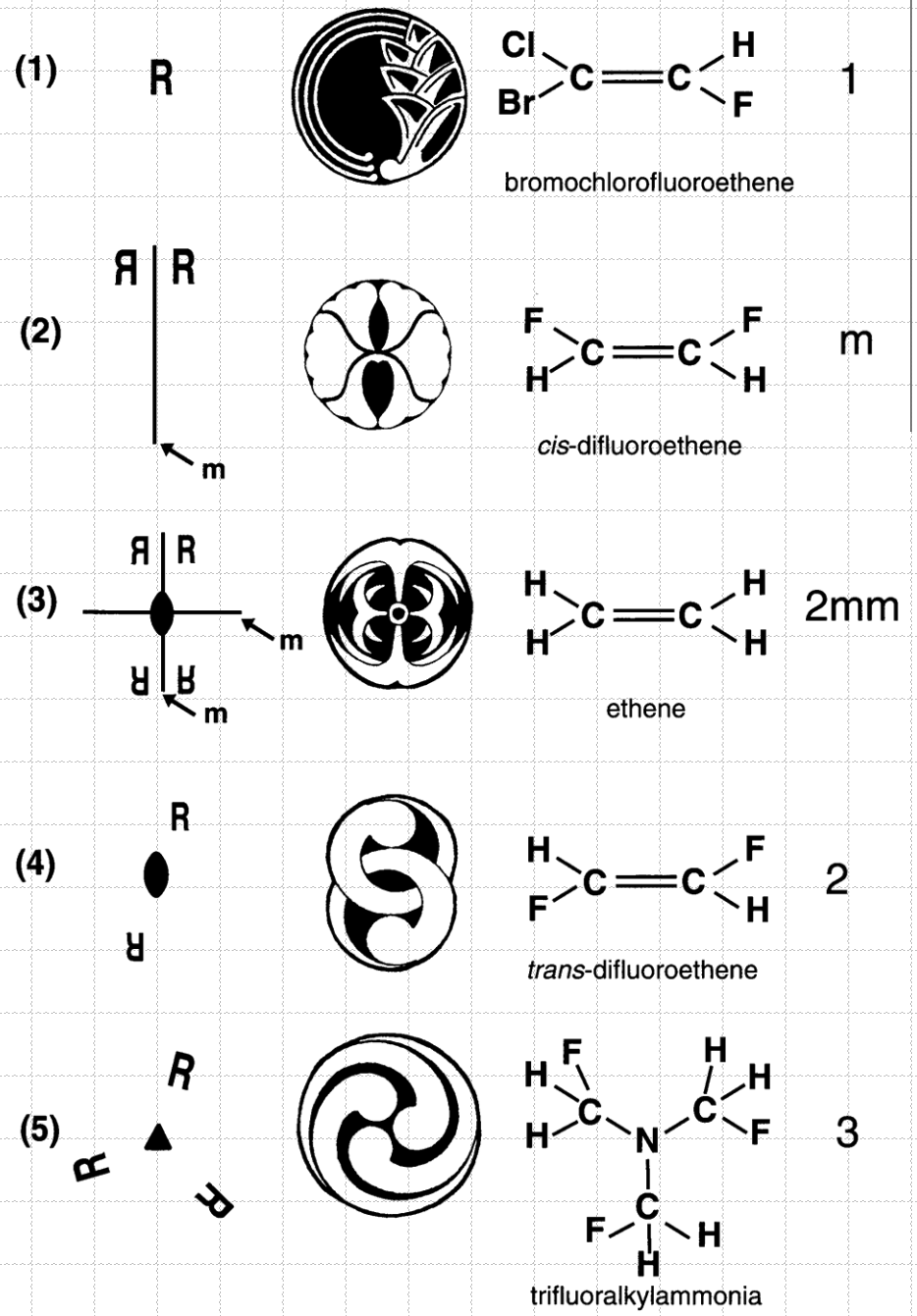
Mirror reflection



Inversion

Two-dimensional Symmetry Elements

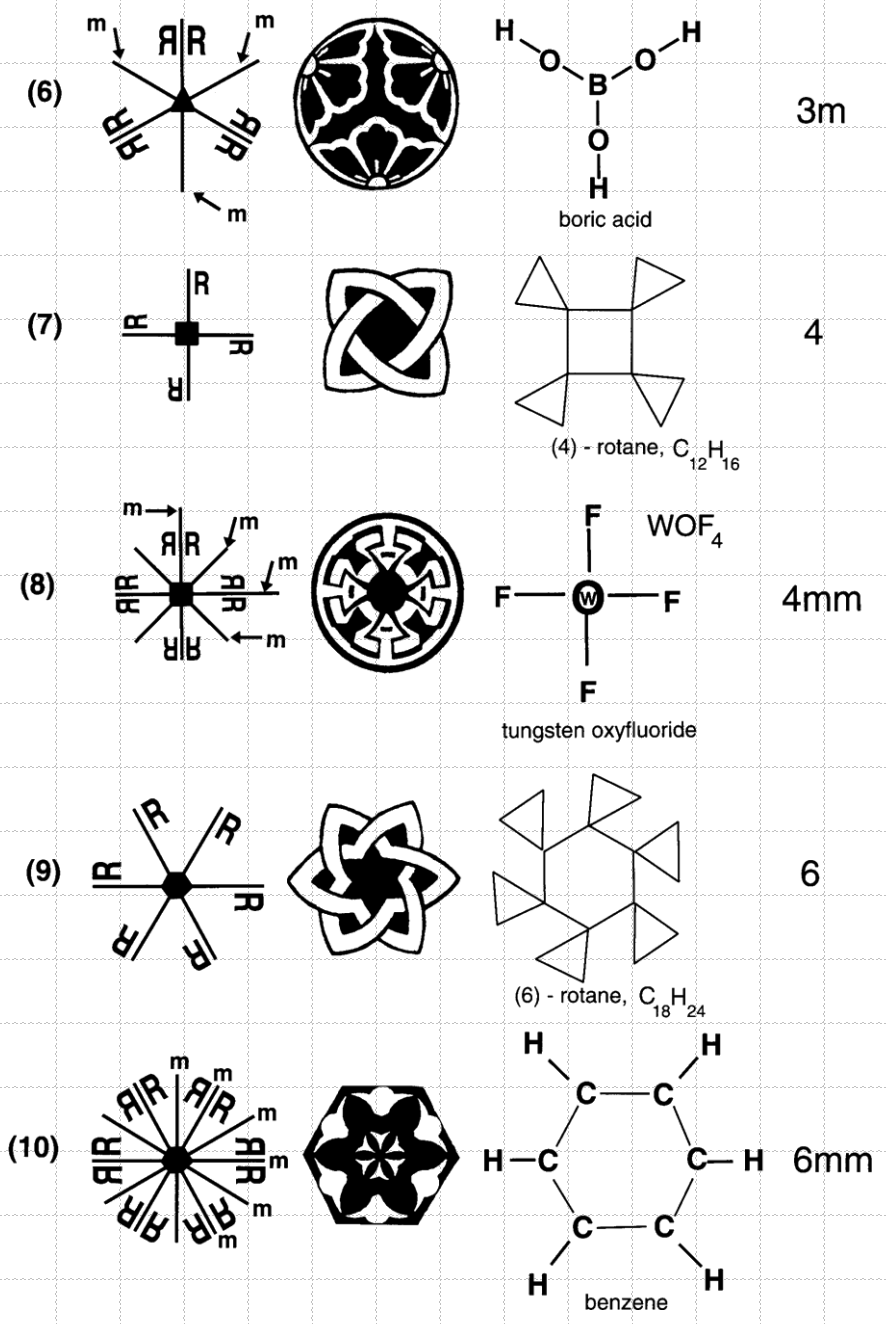
1. One-fold axis (no symmetry)
2. Vertical mirror line
3. Vertical and horizontal mirror lines
4. Two-fold rotation axis
5. Three-fold rotation axis



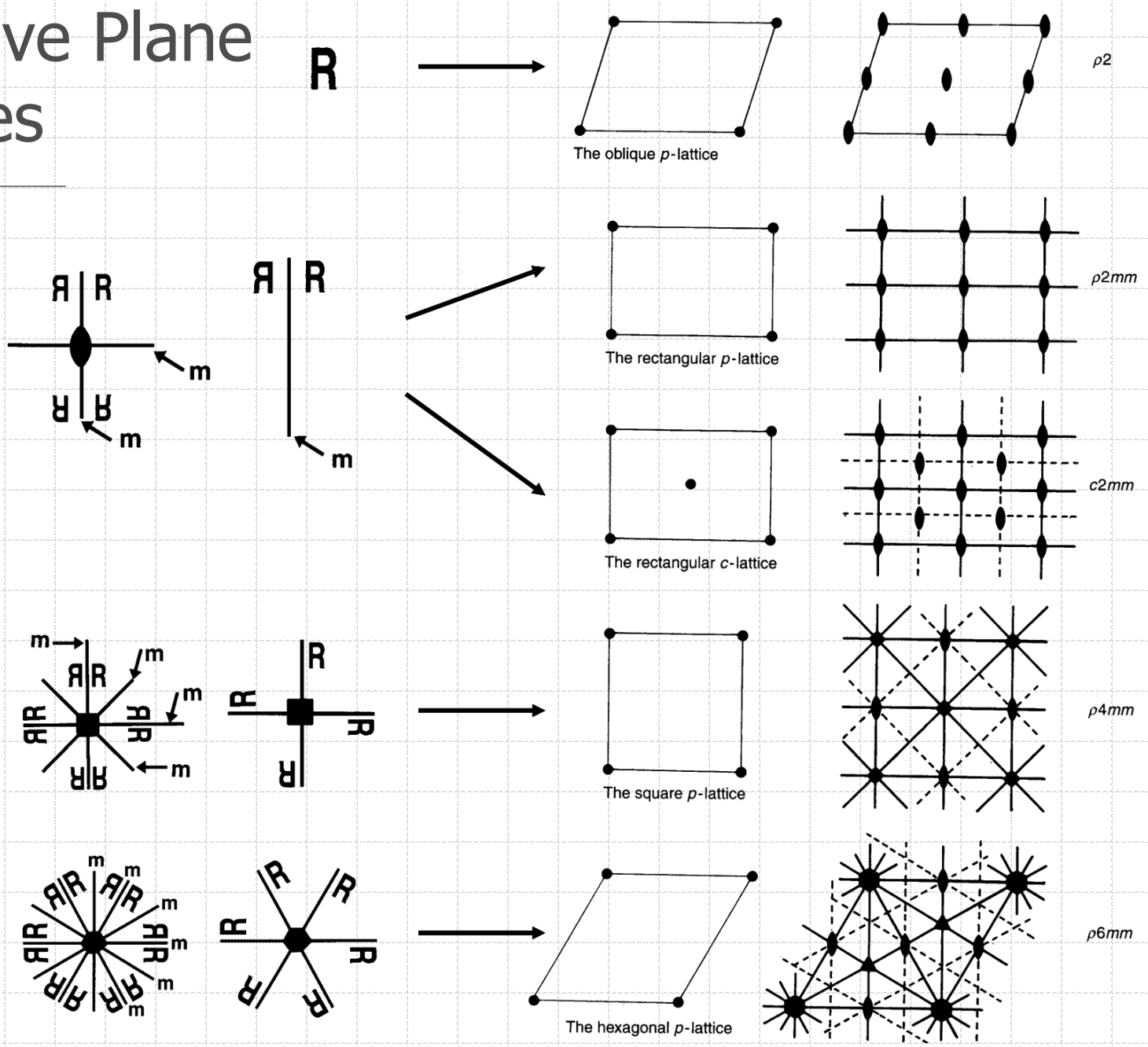
Two-dimensional Symmetry Elements

6. Tree-fold axis + vertical mirror line
7. Four-fold axis
8. Four-fold axis + mirror lines
9. Six-fold axis
10. Six-fold axis + mirror lines

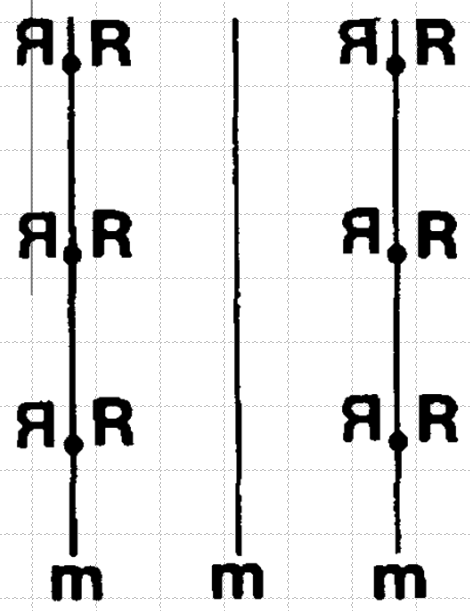
10 two-dimensional crystallographic or plane point groups

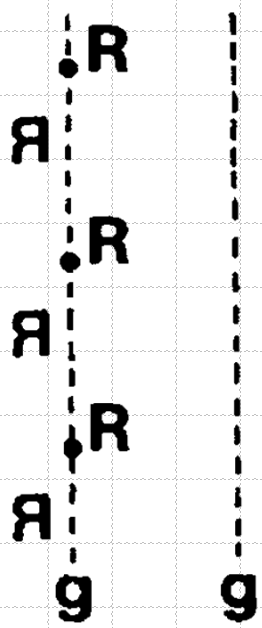


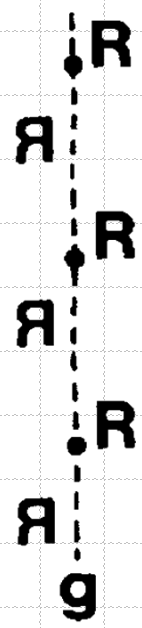
The Five Plane Lattices

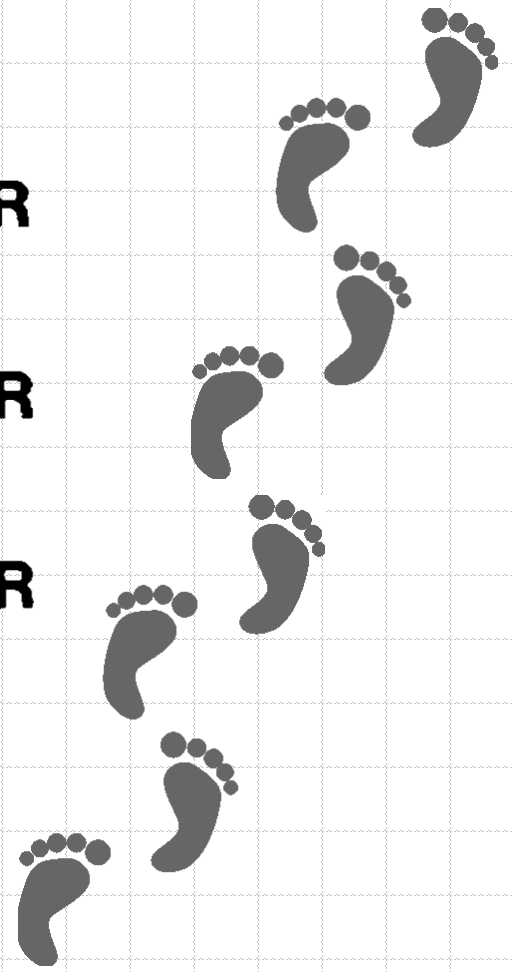


Two-dimensional Symmetry Elements



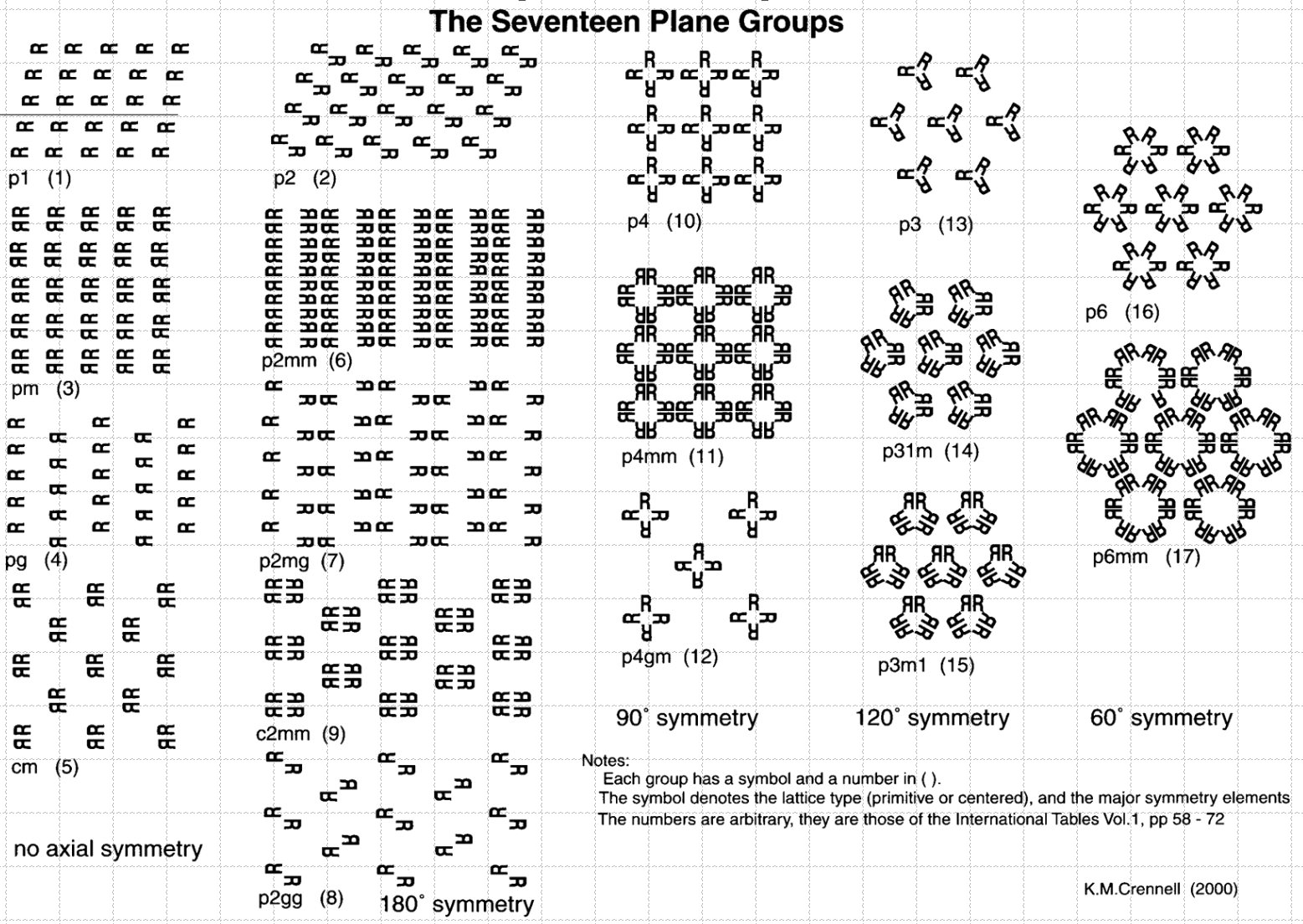




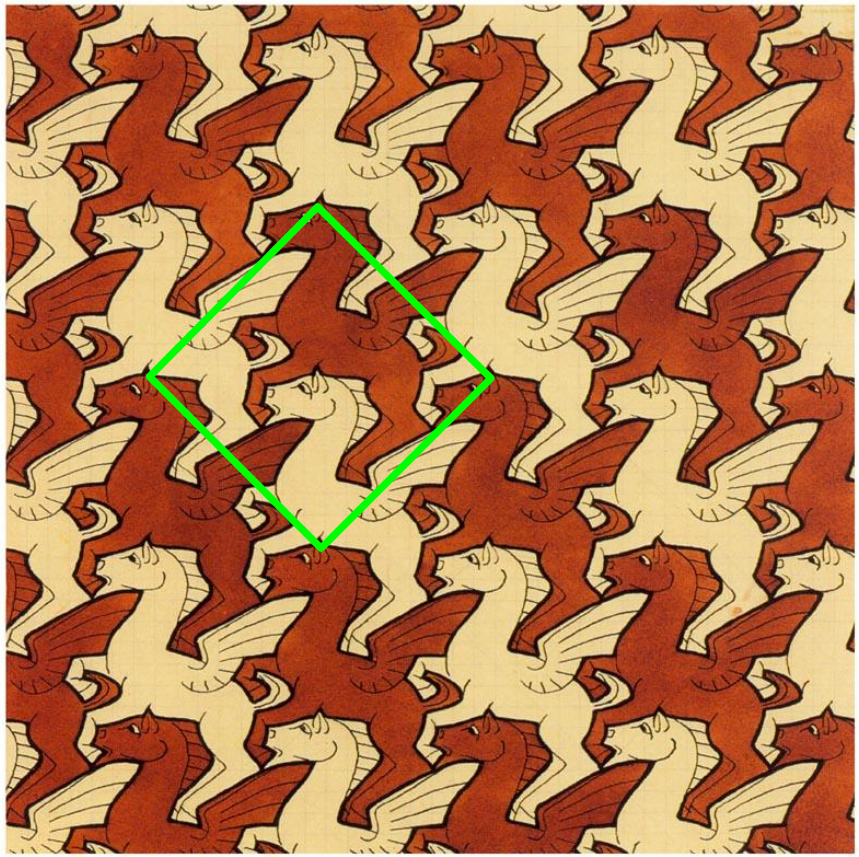


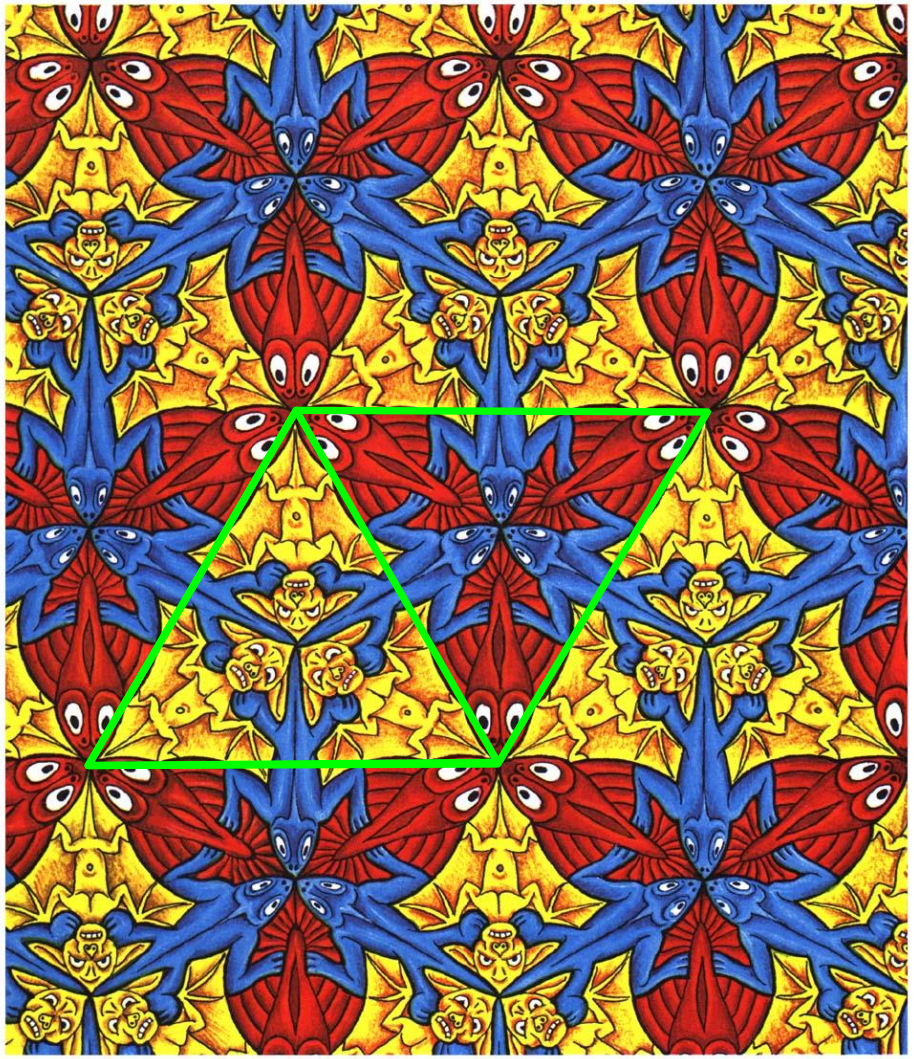
Reflection glide or glide line of symmetry

Two-dimensional Symmetry Elements



Lattice type: *p* for primitive, *c* for centred.
Symmetry elements: *m* for mirror lines, *g* for glide lines, 4 for 4-fold axis etc.





Design by M.C. Escher

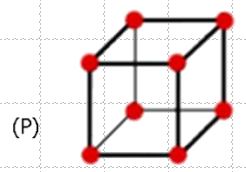
Bravais Lattices and Crystal Systems

- In three dimensions: point symmetry elements and translational symmetry elements.
- For point symmetry elements:
  - centers of symmetry
  - mirror planes
  - inversion axes
- For translational symmetry elements:
  - glide planes
  - screw axes

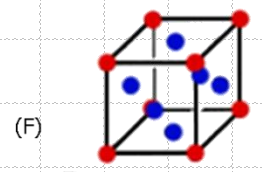
We end up with 230 space groups (was 17 plane groups) **distributed among 14 space lattices** (was 5 plane lattices) **and 32 point group symmetries** (instead of 10 plane point symmetries)

The 14 Space (Bravais) Lattices

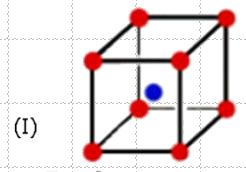
- The systematic work was done by Frankenheim in 1835. Proposed 15 space lattices.
- In 1848 Bravais pointed that two of his lattices were identical (unfortunate for Frankenheim).
- Today we have 14 Bravais lattices.



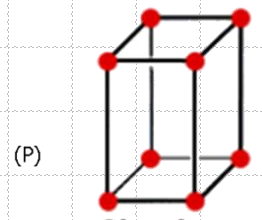
Simple cubic



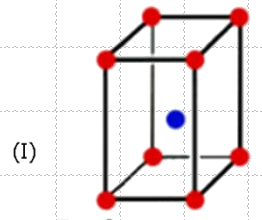
Face-centered cubic



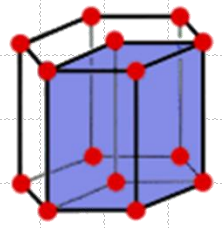
Body-centered cubic



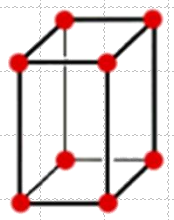
Simple tetragonal



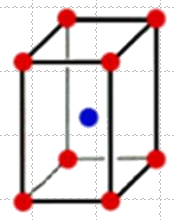
Body-centered tetragonal



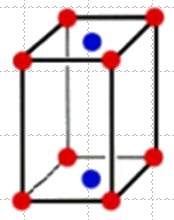
Hexagonal



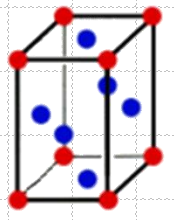
Simple orthorhombic



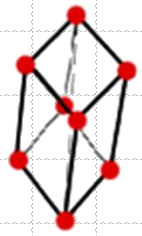
Body-centered orthorhombic



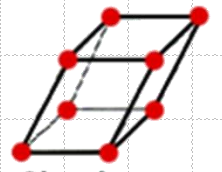
Base-centered orthorhombic



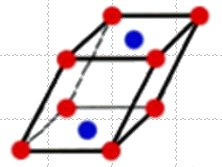
Face-centered orthorhombic



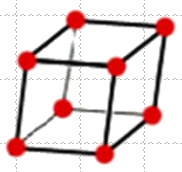
Rhombohedral



Simple Monoclinic



Base-centered monoclinic



Triclinic

a, *b*, *c* – unit cell lengths; α, β, γ - angles between them

Crystal Symmetry

Centering of the lattice	Lattice points per unit cell	International symbol	Lattice translation(s) due to centering
Primitive	1	P	None
Base-centered	2	A	1/2(**b**+**c**)
Base-centered	2	B	1/2(**a**+**c**)
Base-centered	2	C	1/2(**a**+**b**)
Body-centered	2	I	1/2(**a**+**b**+**c**)
Face-centered	4	F	1/2(**b**+**c**); 1/2(**a**+**c**); 1/2(**a**+**b**)
Rhombohedral	3	R	1/3**a**+2/3**b**+2/3**c**; 2/3**a**+1/3**b**+1/3**c**

The 14 Space (Bravais) Lattices

System	Axial lengths and angles	Bravais lattice	Lattice symbol
Cubic	Three equal axes at right angles $a = b = c, \quad \alpha = \beta = \gamma = 90°$	Simple Body-centered Face-centered	P I F
Tetragonal	Three axes at right angles, two equal $a = b \neq c, \quad \alpha = \beta = \gamma = 90°$	Simple Body-centered	P I
Orthorhombic	Three unequal axes at right angles $a \neq b \neq c, \quad \alpha = \beta = \gamma = 90°$	Simple Body-centered Base-centered Face-centered	P I C F
Rhombohedral*	Three equal axes, equally inclined $a = b = c, \quad \alpha = \beta = \gamma \neq 90°$	Simple	R
Hexagonal	Two equal coplanar axes at 120°, third axis at right angles $a = b \neq c, \quad \alpha = \beta = 90° \quad (\gamma = 120°)$	Simple	P
Monoclinic	Three unequal axes, one pair not at right angles $a \neq b \neq c, \quad \alpha = \gamma = 90° \neq \beta$	Simple Base-centered	P C
Triclinic	Three unequal axes, unequally inclined and none at right angles $a \neq b \neq c, \quad (\alpha \neq \beta \neq \gamma \neq 90°)$	Simple	P

* Also called trigonal.

7 crystal systems

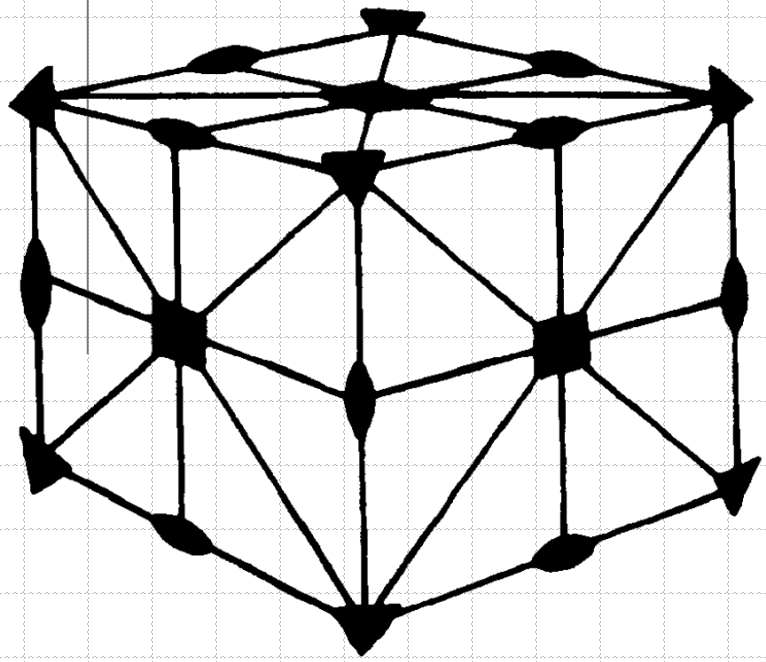
Crystal Symmetry

- 7 axial systems + 32 point groups $\rightarrow$ 230 unique space groups
- A 3-D crystal must have one of these 230 arrangements, but the atomic coordinates (i.e. occupied equipoints) may be very different between different crystals

Crystal Class	Non-centrosymmetric Point Group	Centrosymmetric Point Group	Minimum Rotational Symmetry
Triclinic	1	$\bar{1}$	One 1-fold
Monoclinic	$2, m$	$2/m$	One 2-fold
Orthorombic	$222, mm2$	mmm	Three 2-folds
Tetragonal	$4, 422, \bar{4}, 4mm, \bar{4}2m$	$4/m, 4/mmm$	One 4-fold
Trigonal	$3, 32, 3m$	$\bar{3}, \bar{3}m$	One 3-fold
Hexagonal	$6, 622, \bar{6}, 6mm, \bar{6}m2$	$6/m, 6/mmm$	One 6-fold
Cubic	$23, 432, \bar{4}3m$	$m\bar{3}, m\bar{3}m$	Four 3-folds

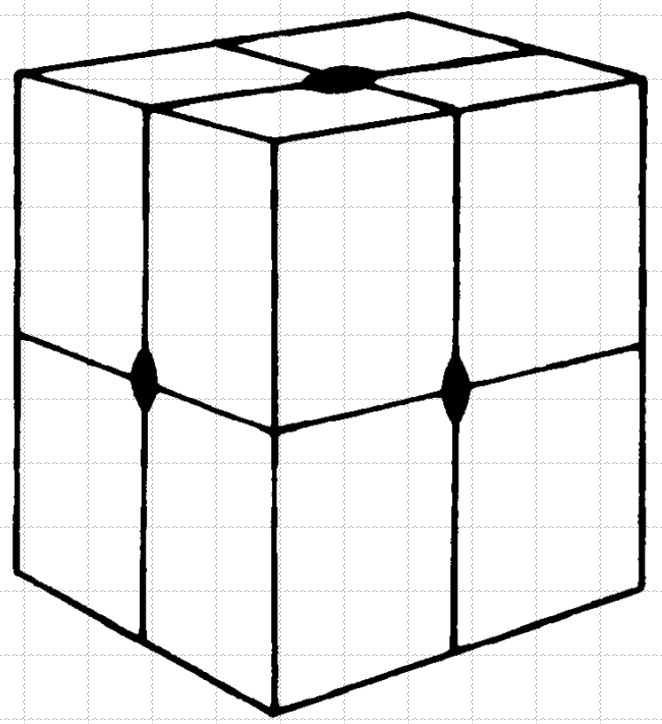
The Symmetry of Bravais Lattices

Point group symmetry of the cube



- Nine mirror planes
- Three four-fold axes
- Four three-fold axes
- Six two-fold axes

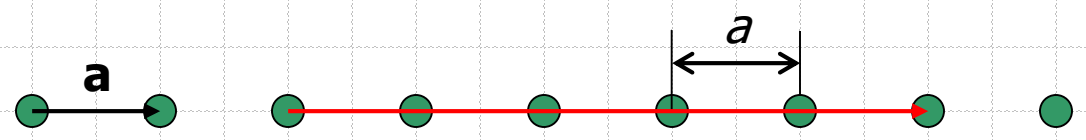
Point group symmetry of the orthorhombic cell



- Three mirror planes
- Three two-fold axes

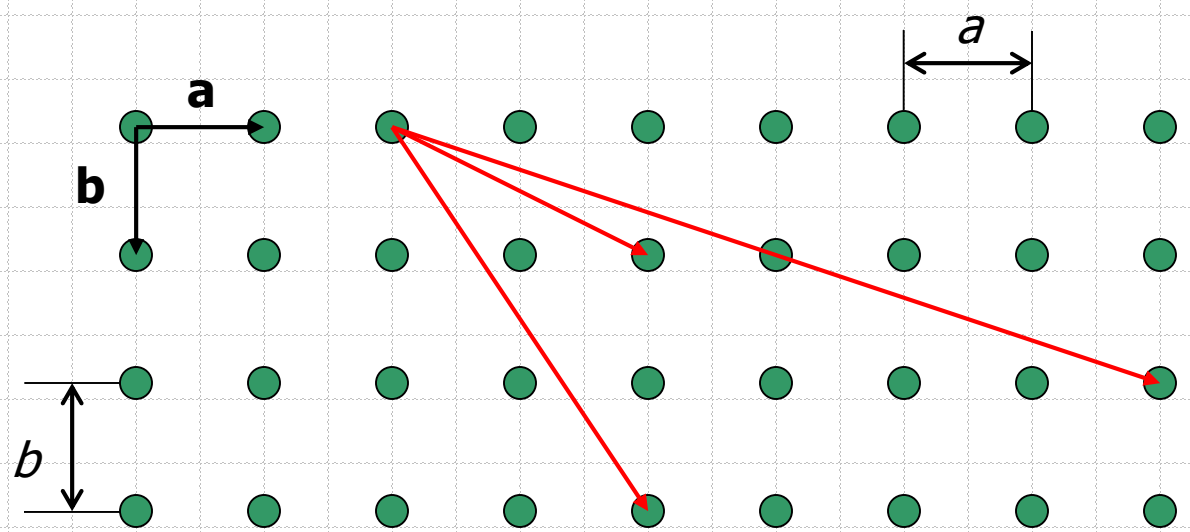
Crystal Axes and the Reciprocal Lattice

Crystal Lattice & Directions



$$\mathbf{r} = u\mathbf{a}$$

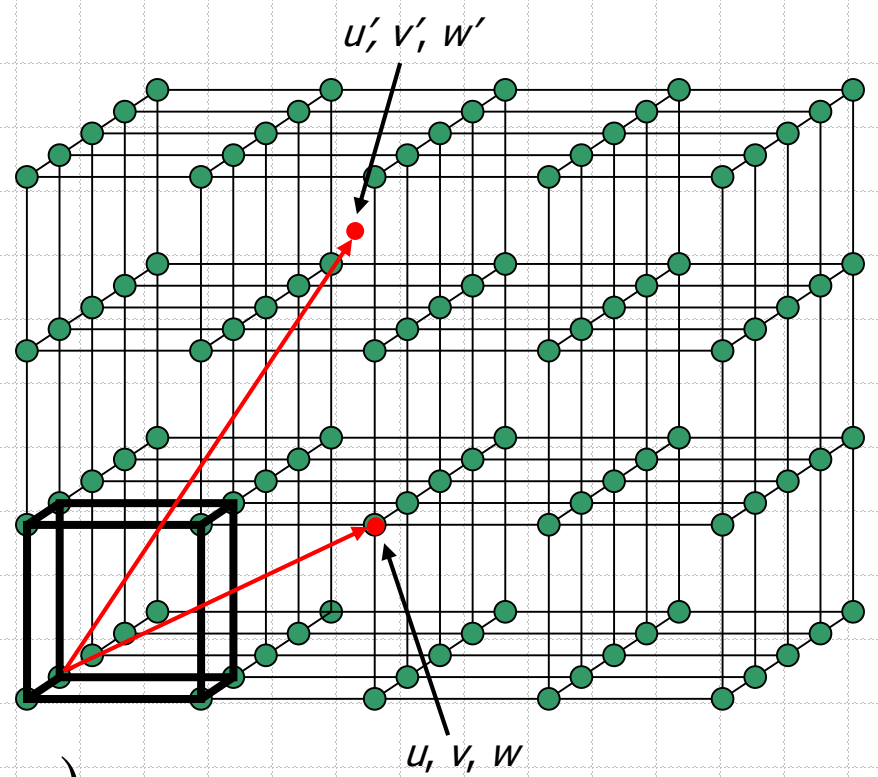
One-dimensional lattice with parameter *a*



$$\mathbf{r} = u\mathbf{a} + v\mathbf{b}$$

Two-dimensional lattice with parameters *a* and *b*

Lattice Directions



For the lattice points u, v, w:

$$\mathbf{r} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$$

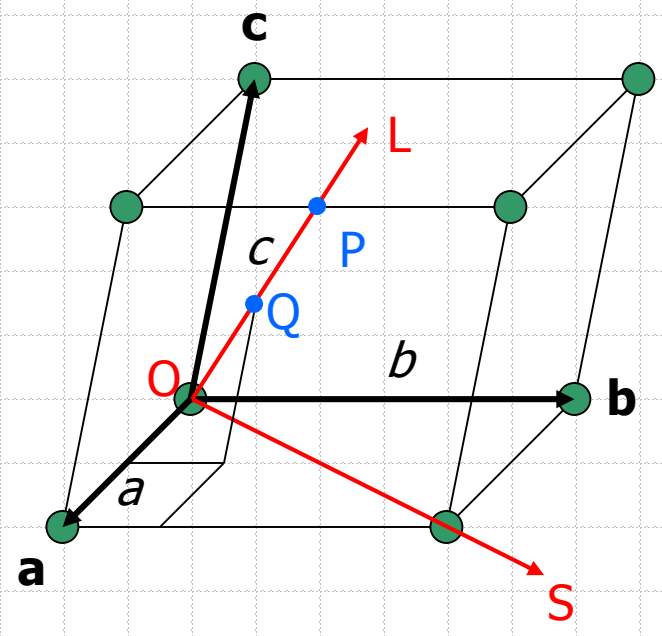
For the points in space u', v', w' that are not lattice points:

$$\mathbf{r} = u'\mathbf{a} + v'\mathbf{b} + w'\mathbf{c}$$
$$= (n + u_1)\mathbf{a} + (p + v_1)\mathbf{b} + (q + w_1)\mathbf{c}$$
$$= (n\mathbf{a} + p\mathbf{b} + q\mathbf{c}) + (u_1\mathbf{a} + v_1\mathbf{b} + w_1\mathbf{c})$$

n, p, q – integers
u_1, v_1, w_1 – fractions

Indexing Lattice Directions

- Direction must pass through the origin
- Coordinates of point P (in fractions of *a*, *b* and *c*) are 1, ½, 1 ⇒ [212]
- For point Q coordinates are ½, ¼, ½ ⇒ [212]



[212] – defines direction for OL

For OS – the direction is [110]

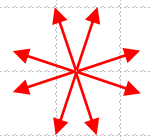
$$\mathbf{r}_{102} = 2\mathbf{a} + 1\mathbf{b} + 2\mathbf{c}$$

$$\mathbf{r}_{110} = 1\mathbf{a} + 1\mathbf{b} + 0\mathbf{c}$$

Indexing Lattice Directions

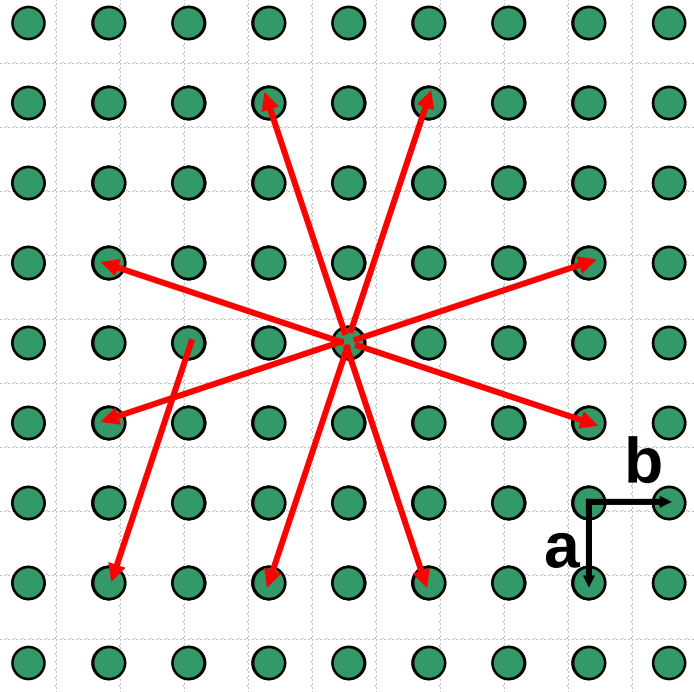
- Specific direction ⇒ [*uvw*] Family of directions ⇒ <*uvw*>

Example:



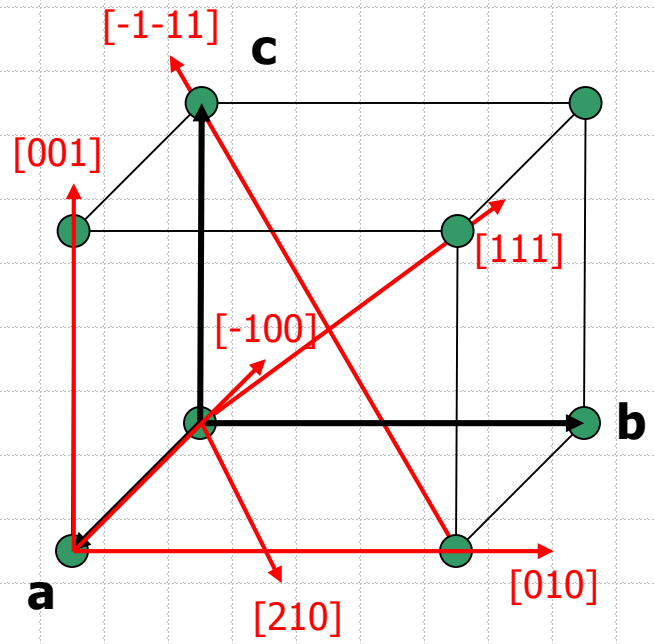
<310>

[3-10]



Indexing Lattice Directions

- Directions related by symmetry are called *directions of a form*.



We have: [111], [-111], [-1-1-1], [11-1], …

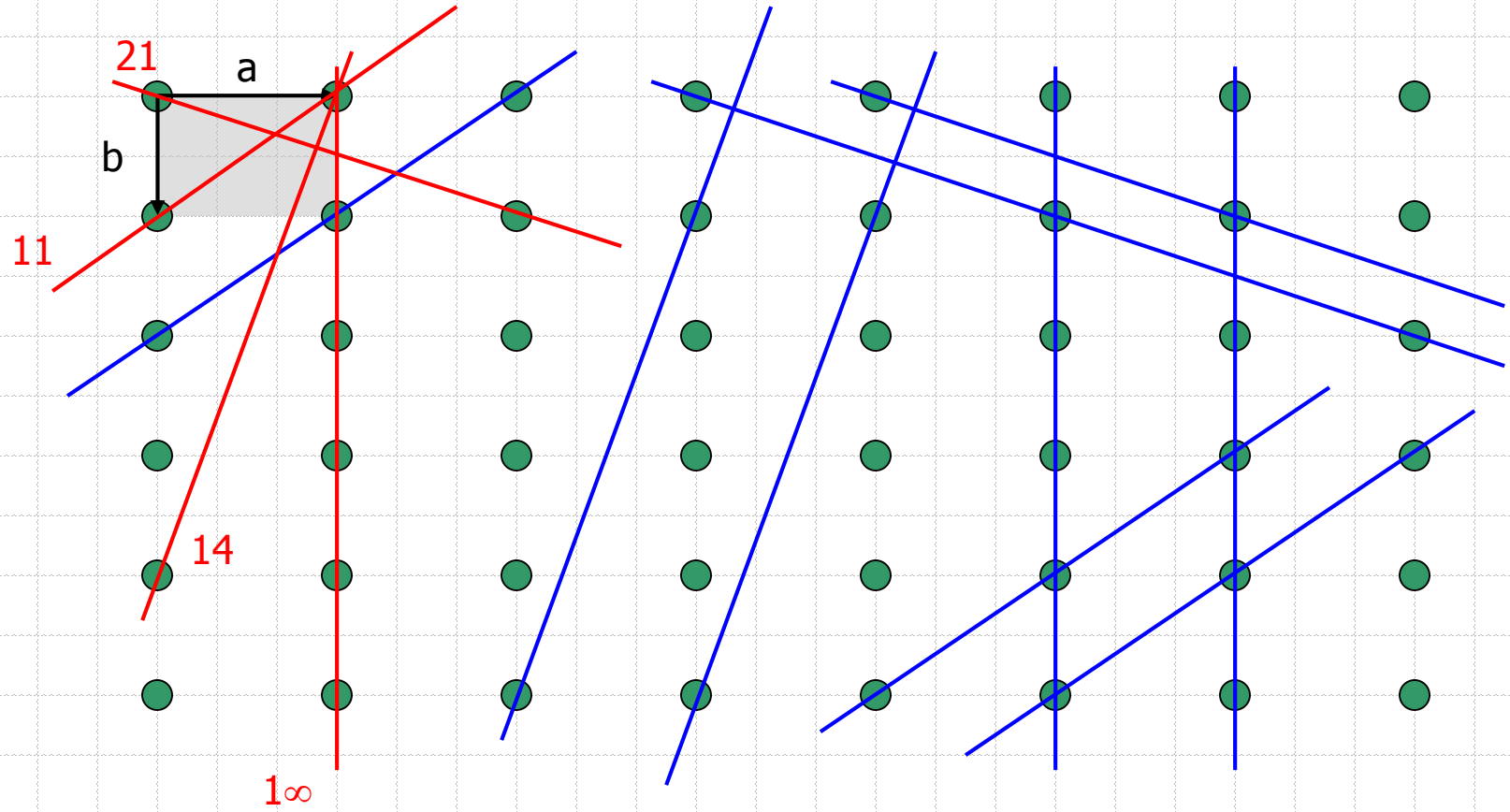
<111>

Specific direction ⇒ [*uvw*]

Family of directions ⇒ <*uvw*>

The Crystallographic Planes

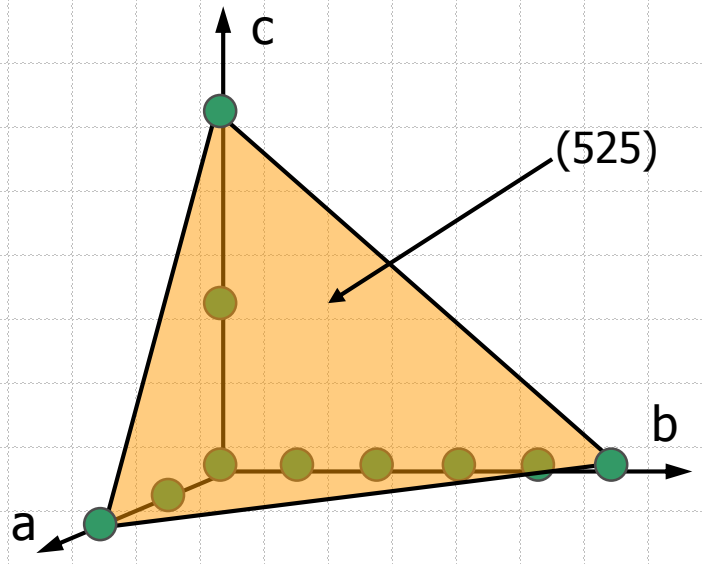
1 1		1 1		(11)
2 1	⇒	1/2 1	=	(12)
1 4		1 1/4		(41)
1 ∞		1 1/∞		(10)



Definition of the Miller Indices

- Let's draw a plane at $2\times a$, $5\times b$, $2\times c$.

	a	**b**	**c**
The intercepts	2	5	2
The reciprocals	1/2	1/5	1/2
Multiply by 10	5	2	5
The Miller indices	(525)		

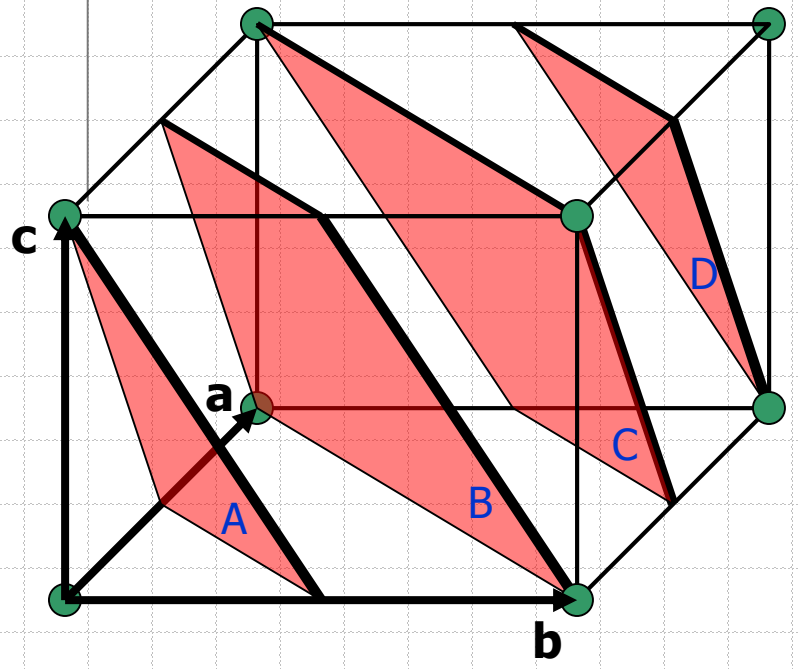


Specific plane $\Rightarrow$ (*hkl*)

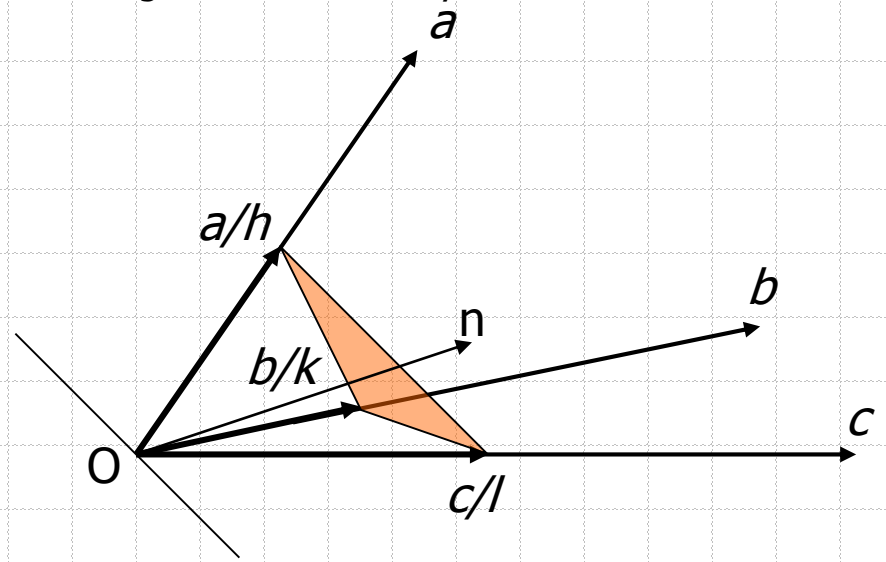
Family of planes $\Rightarrow$ {*hkl*}

Definition of the Miller Indices

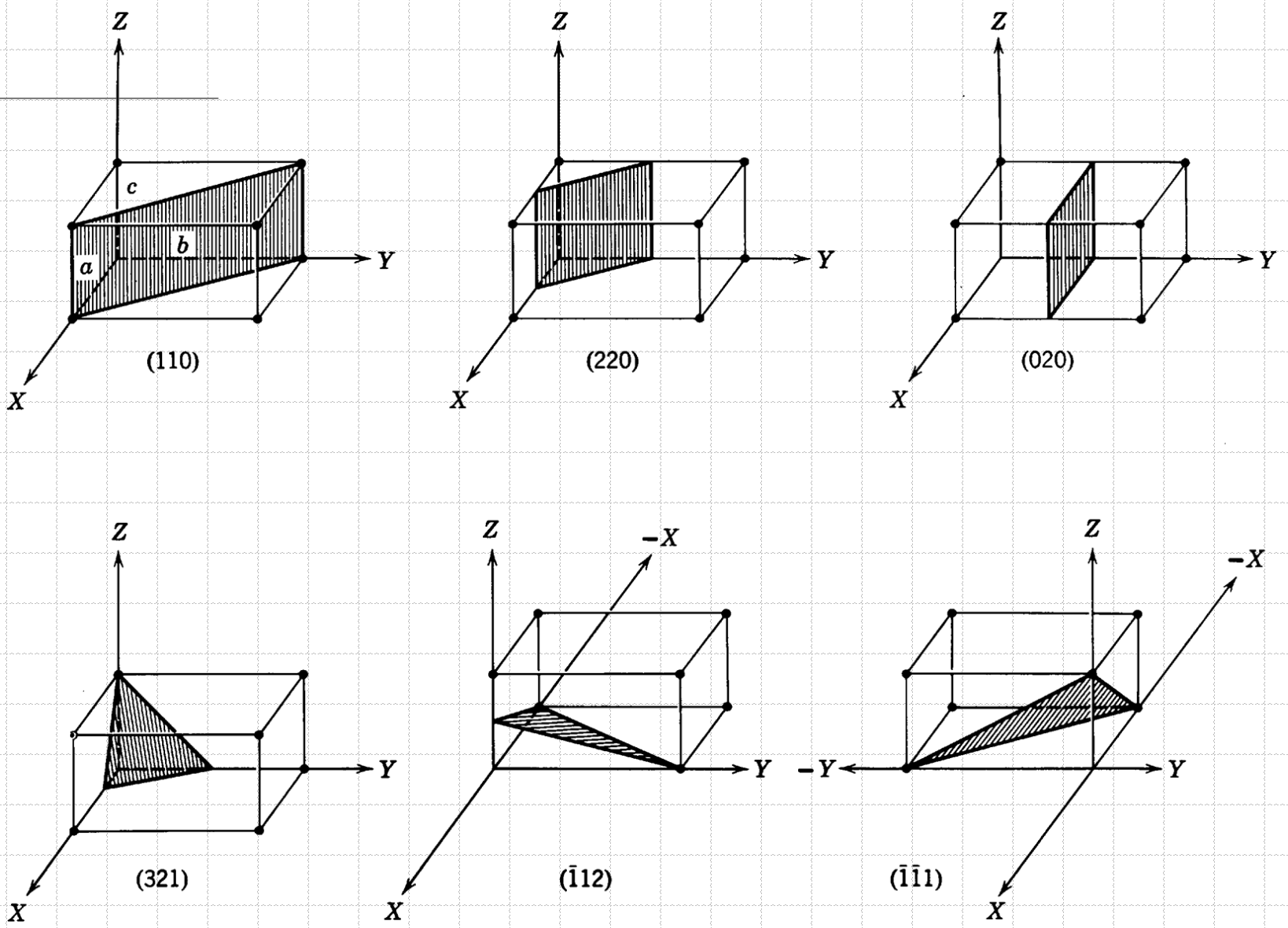
- For plane A $a/2$, $b/2$, and $1c \Rightarrow$ 2, 2, 1 $\Rightarrow$ plane is (221)
- For plane B $1a$, $1b$, and $2c \Rightarrow$ 1, 1, 1/2 $\Rightarrow$ 2, 2, 1 $\Rightarrow$ plane is (221)
- For plane C $3a/2$, $3b/2$, and $3c \Rightarrow$ 2/3, 2/3, 1/3 $\Rightarrow$ 2, 2, 1 $\Rightarrow$ plane is (221)
- For plane D $2a$, $2b$, and $4c \Rightarrow$ 1/2, 1/2, 1/4 $\Rightarrow$ 2, 2, 1 $\Rightarrow$ plane is (221)



- By the set of crystallographic planes *hkl*, we mean a set of parallel equidistant planes, one of which passes through the origin, and the next nearest makes intercepts *a/h*, *b/k*, and *c/l* on the three crystallographic axes.
- The integers *hkl* are usually called the Miller indices.



Miller Indices



Miller Indices and Zone Axis Symbols

Closures for crystallographic indices

[*uvw*] = square brackets designate a direction in the lattice from the origin to a point. Used to collectively include all the faces of a crystals whose intersects (i.e., edges) parallel each other. These are referred to as crystallographic **zones** and they represent a direction in the crystal lattice.

<*uvw*> – designate family of directions.

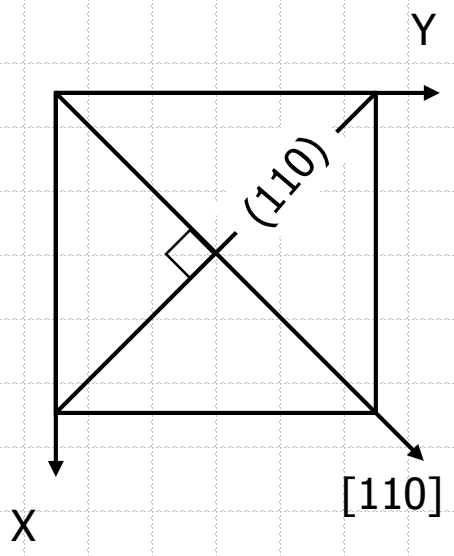
(*hkl*) = parenthesis designate a *crystal face* or a *family of planes* throughout a crystal lattice.

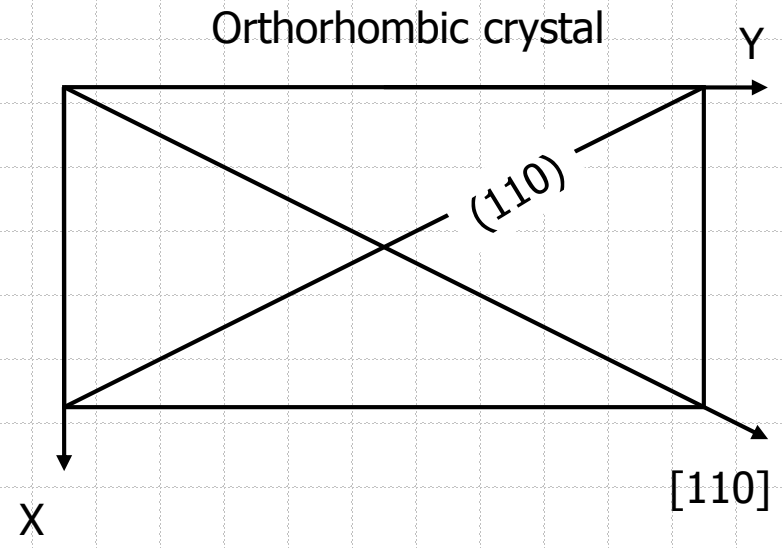
{*hkl*} = "squiggly" brackets or braces designate a set of faces that are equivalent by the symmetry of the crystal. The set of face planes results in the **crystal form**. {100} in the isometric class includes (100), (010), (001), (-100), (0-10) and (00-1), while for the triclinic {100} only the (100) is included.

d-spacing is defined as the distance between adjacent planes. When X-rays diffract due to interference amongst a family of similar atomic planes, then each diffraction plane may be reference by it's indices d_{hkl}

Miller Indices and Zone Axis Symbols

- For cubic crystal:
  - Direction symbols
    - <100> ⇒ [100], [-100], [010], 0 -10], [001], [00 -1]
    - <111> ⇒ [11 -1], [-1 -11], [1 -11], [-11 -1], [-111], [1 -1 -1], [111], [-1 -1 -1]
    - <110> ⇒ 12 combinations
  - Miller indices
    - {100} ⇒ (100), (-100), (010), (0 -10), (001), (00 -1)





Lattice Plane Spacings

- For crystal with orthogonal axes:

$$OA\cos\alpha = ON \rightarrow (a/h)\cos\alpha = d_{hkl} \rightarrow \cos\alpha = \left(\frac{h}{a}\right)d_{hkl}$$

- For angles β and γ:

$$\cos\beta = \left(\frac{k}{b}\right)d_{hkl}$$

$$\cos\gamma = \left(\frac{l}{c}\right)d_{hkl}$$

- Since for orthogonal axes:

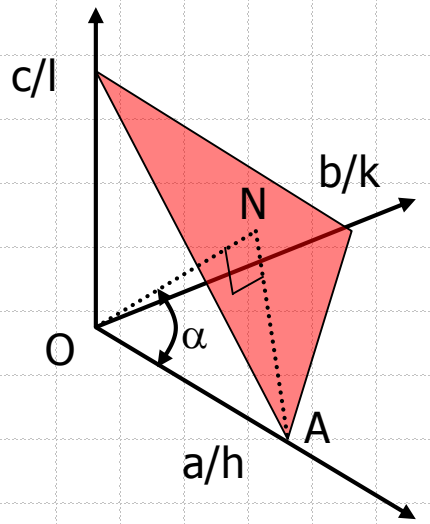
$$\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1$$

- We write:

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

- For a cubic crystal $a = b = c$, hence

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



Lattice plane – (*hkl*)
ON – interplanar spacing

Lattice Plane Spacings

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:

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

Triclinic:

$$\frac{1}{d^2} = \frac{1}{V^2}(S_{11}h^2 + S_{22}k^2 + S_{33}l^2 + 2S_{12}hk + 2S_{23}kl + 2S_{13}hl)$$

V = volume of unit cell

$S_{11} = b^2c^2\sin^2\alpha,$

$S_{22} = a^2c^2\sin^2\beta,$

$S_{33} = a^2b^2\sin^2\gamma,$

$S_{12} = abc^2(\cos\alpha\cos\beta - \cos\gamma),$

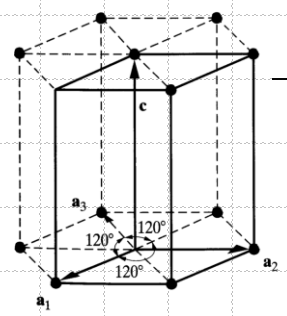
$S_{23} = a^2bc(\cos\beta\cos\gamma - \cos\alpha),$

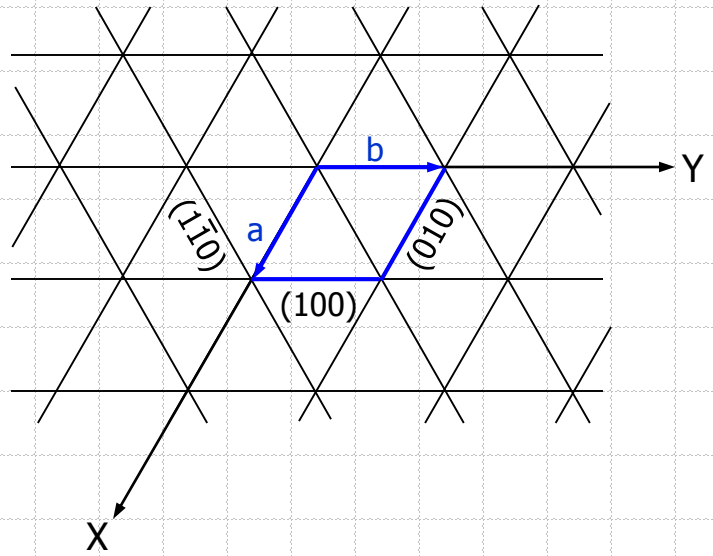
$S_{13} = ab^2c(\cos\gamma\cos\alpha - \cos\beta).$

Special Case: Trigonal & Hexagonal Lattices

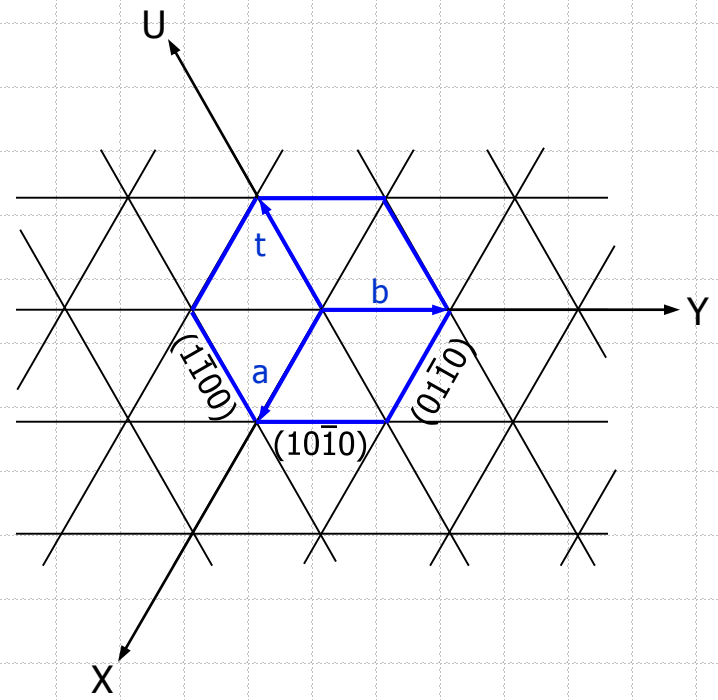
- (1 -10), (100), and (010) are indices different in type but describe crystallographically equivalent lattice planes.
- Introducing the fourth axis – U. We have Miller-Bravais indices (*hkil*).
- All indices of the planes are of the same form – {10 -10}.

$h + k + i = 0 \Rightarrow i = -(h + k) \Rightarrow \{hk.l\}$





(a)



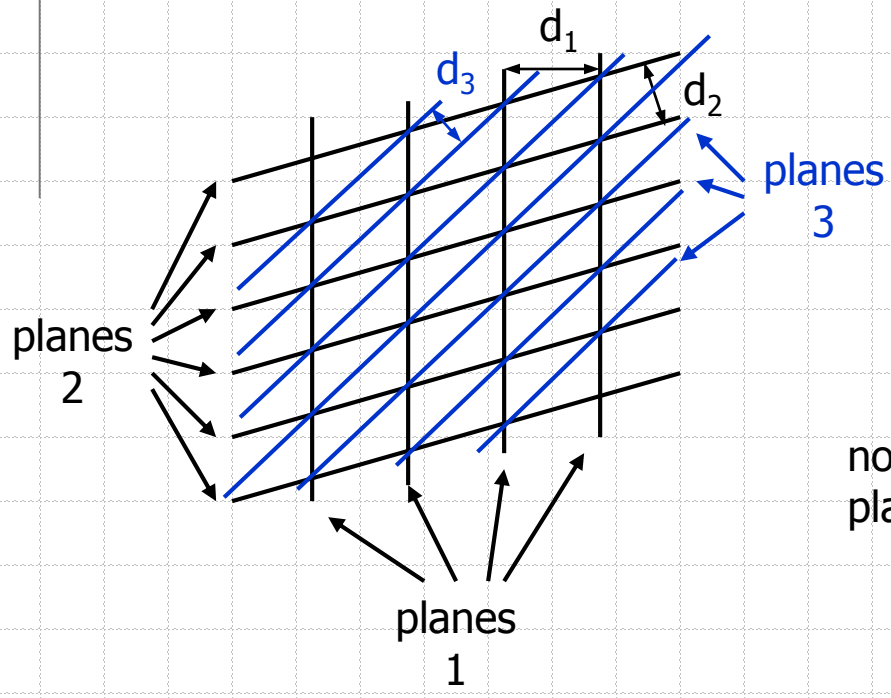
(b)

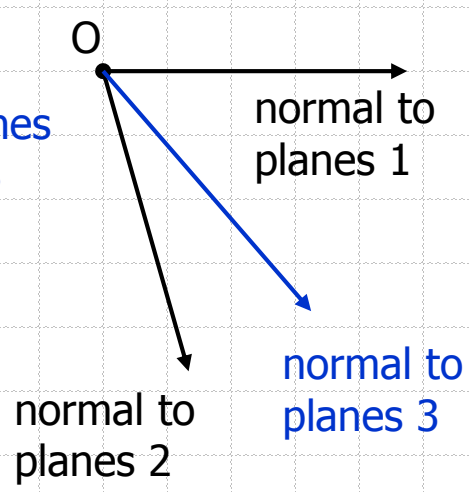
The Reciprocal Lattice

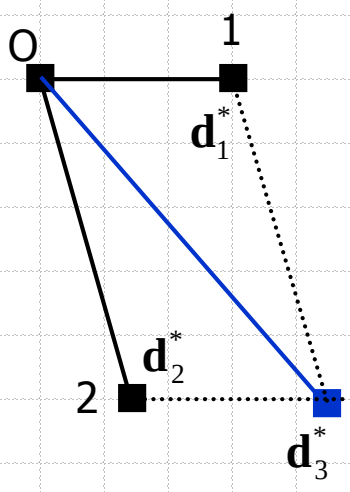
- Reciprocal lattice vectors

$$\mathbf{d}_1^* = K / d_1,$$
$$\mathbf{d}_2^* = K / d_2,$$
$$\mathbf{d}_3^* = K / d_3$$

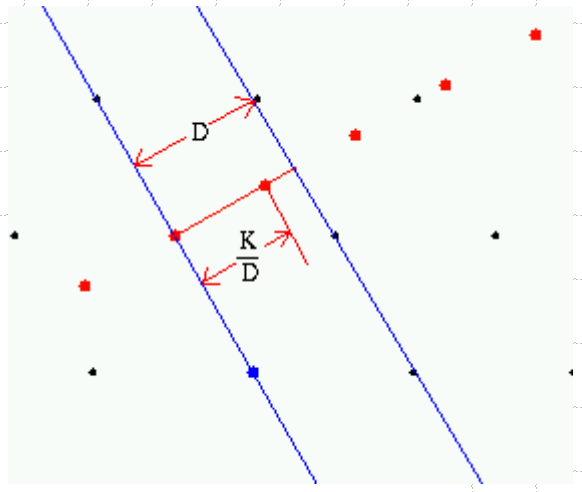
K – is a constant

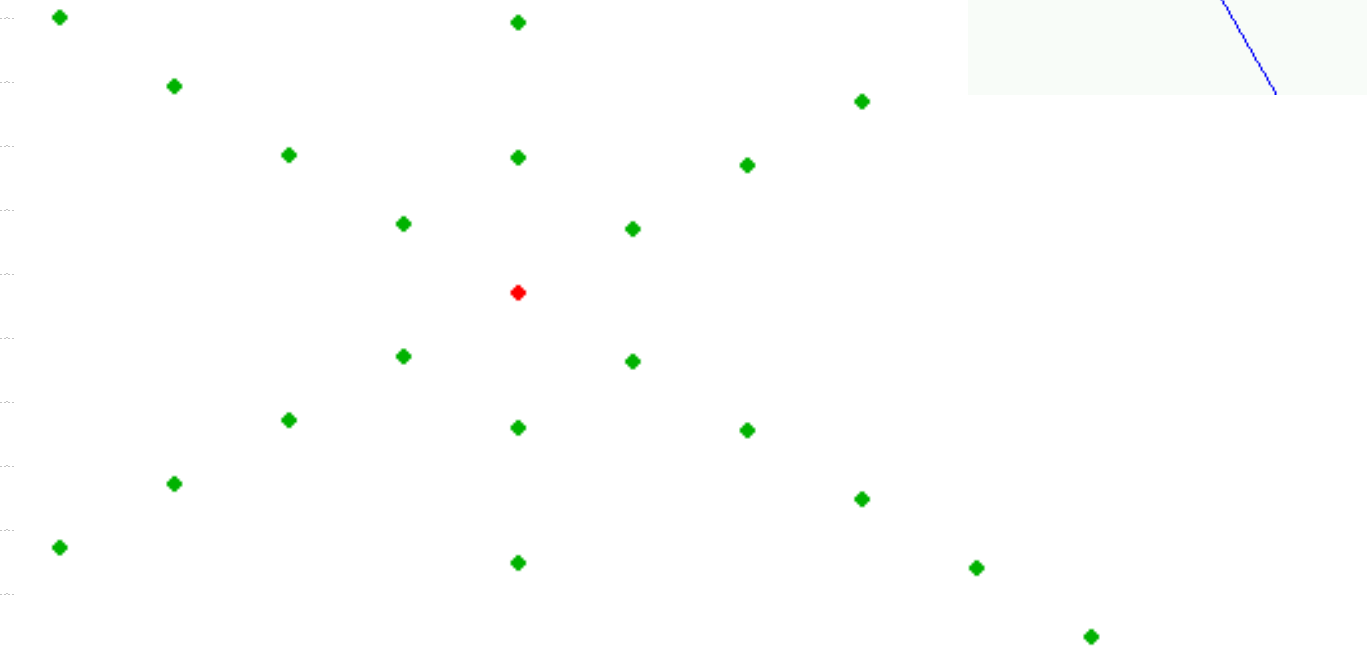




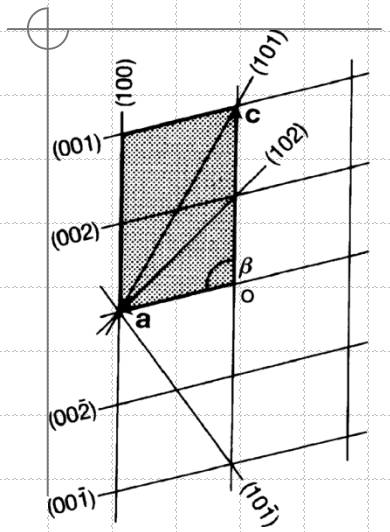


The Reciprocal Lattice

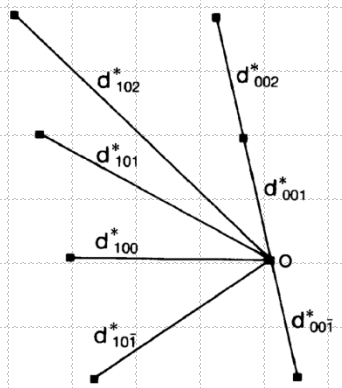




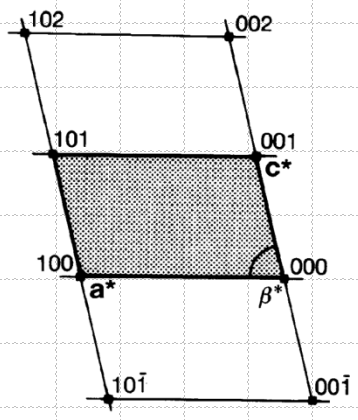
The Reciprocal Lattice



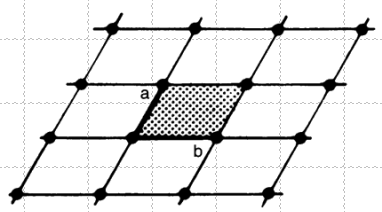
Monoclinic unit cell planes $\{h\,0\,l\}$

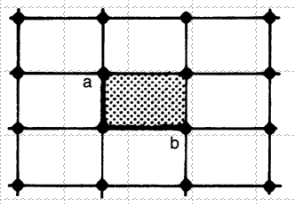


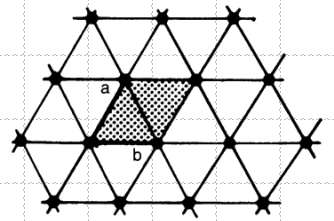
Reciprocal lattice vectors

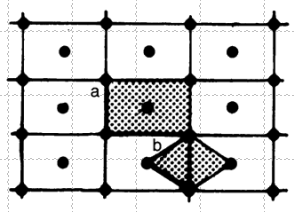


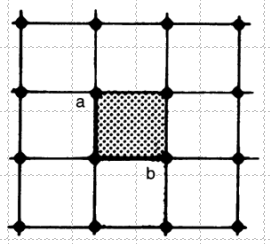
Reciprocal lattice unit cell

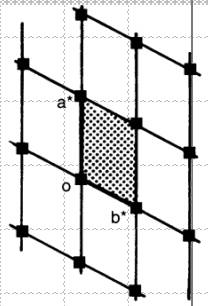


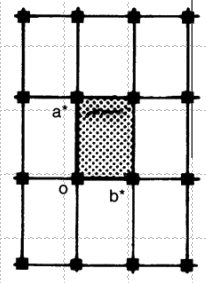


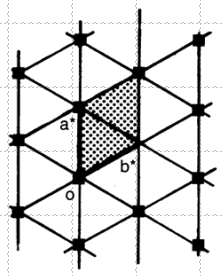


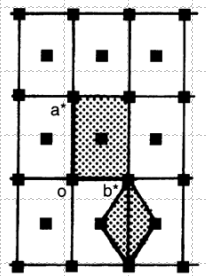


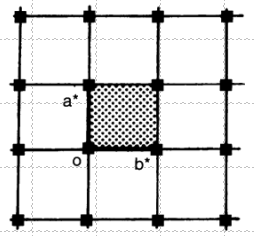








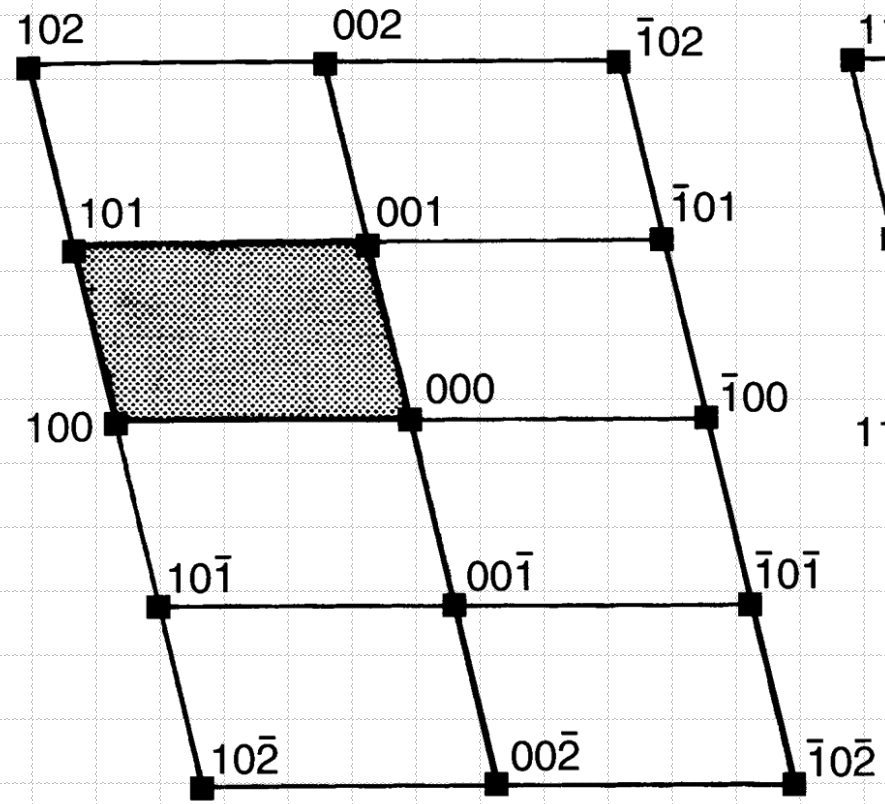




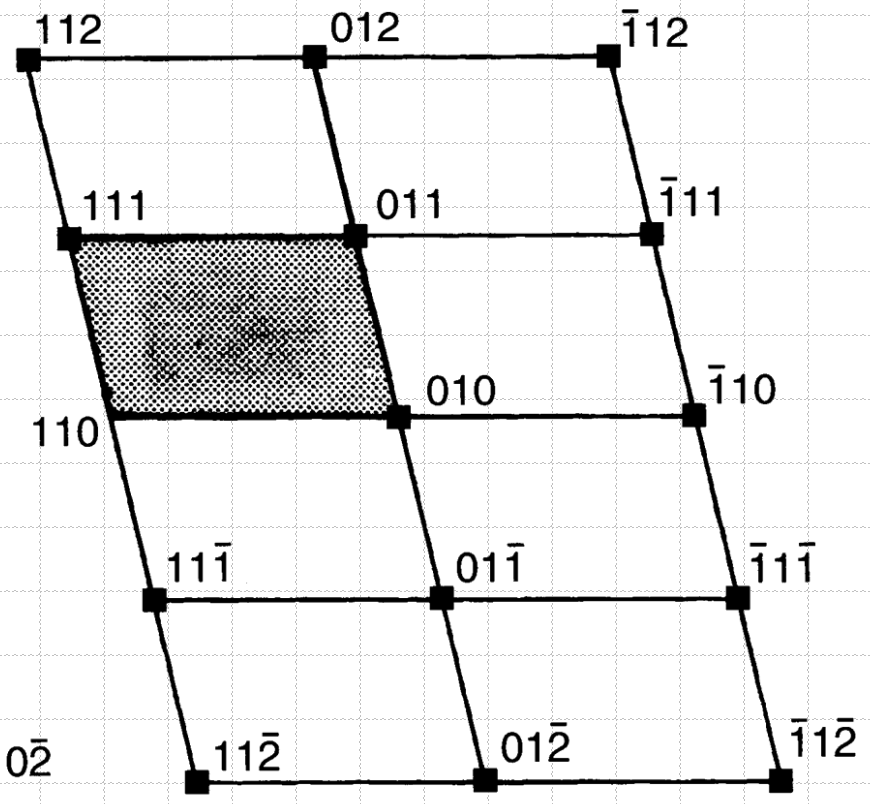
$$\mathbf{a}^* = \mathbf{d}^*_{100} \text{ and } \left|\mathbf{a}^*\right| = 1/d_{100};$$

$$\mathbf{c}^* = \mathbf{d}^*_{001} \text{ and } \left|\mathbf{c}^*\right| = 1/d_{001}$$

The Reciprocal Lattice



h0l section



h1l section

The Reciprocal Lattice

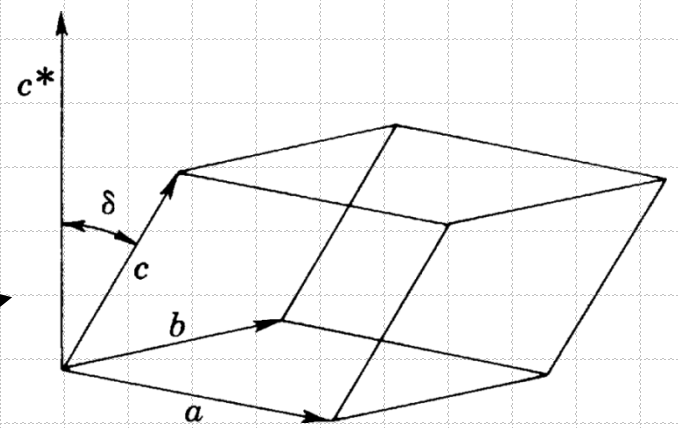
- Consider a real space unit cell with real lattice basis vectors **a**, **b** and **c**
- We define a set of reciprocal lattice basis vectors by:

$$\mathbf{a}^* = \frac{1}{V}(\mathbf{b}\times\mathbf{c}) = \frac{\mathbf{b}\times\mathbf{c}}{\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c})}$$

volume of real space unit cell

$$\mathbf{b}^* = \frac{1}{V}(\mathbf{c}\times\mathbf{a})$$

$$\mathbf{c}^* = \frac{1}{V}(\mathbf{a}\times\mathbf{b})$$



c ⊥ a-b plane*

The Reciprocal Lattice

- Just like we can define a real space lattice in terms of our real space lattice vectors, we can define a reciprocal space lattice in terms of our reciprocal space lattice vectors:

$$\mathbf{r}^* = \mathbf{d}^*_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$$

The real and reciprocal space lattice vectors form an orthonormal set:

$$\left.\begin{aligned} \mathbf{a}^* \cdot \mathbf{b} = \mathbf{a}^* \cdot \mathbf{c} = 0 \\ \mathbf{a}^* \cdot \mathbf{a} = 1 \end{aligned}\right\}$$ similar for $\boldsymbol{b}^*$ and $\boldsymbol{c}^*$

We can define a reciprocal unit cell with volume $\boldsymbol{V}^*$:

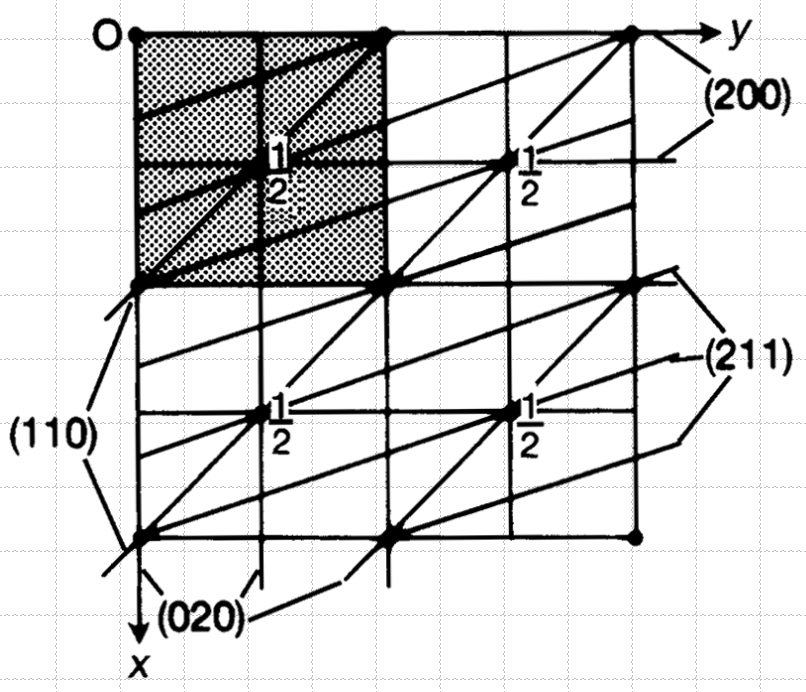
$$V^* = \mathbf{a}^* \cdot \left(\mathbf{b}^* \times \mathbf{c}^*\right) \qquad V^* \cdot V = 1$$

- Now we can write:

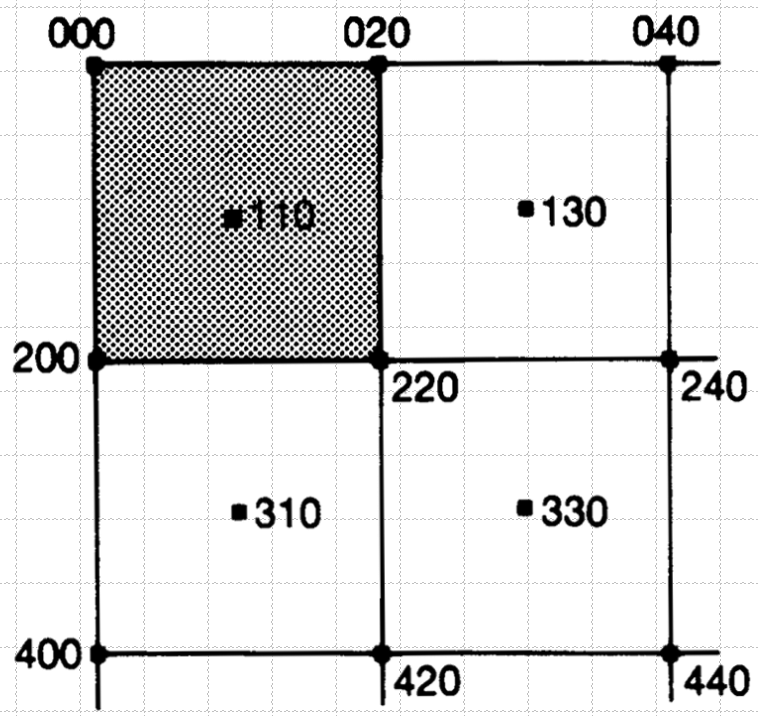
$$\mathbf{r}_{uvw} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$$

$$\mathbf{d}^*_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$$

The Reciprocal Lattice

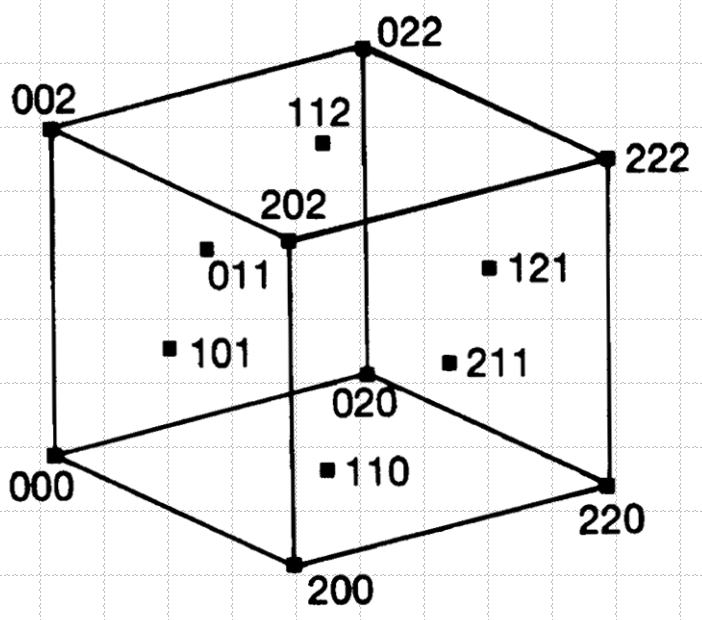


Plan of a cubic *I* crystal ⊥ *z*-axis

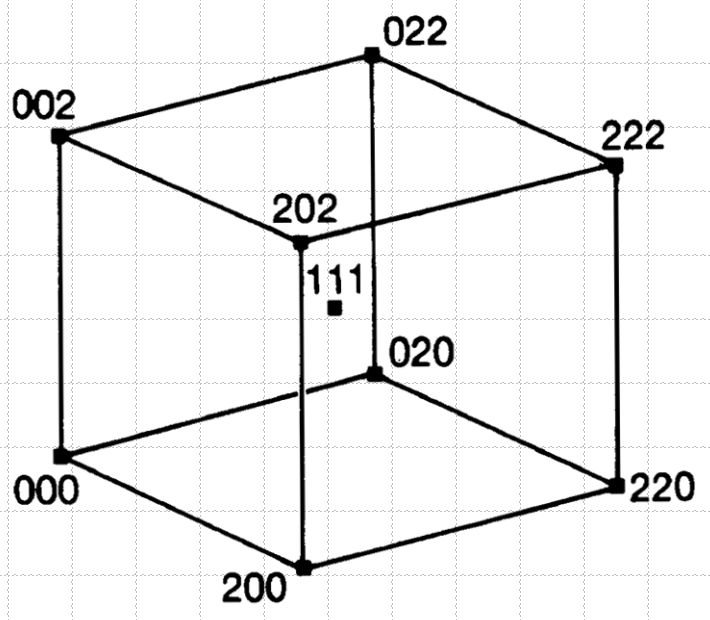


Reciprocal lattice points

The Reciprocal Lattice



Cubic *F* reciprocal lattice unit cell of a cubic *I* direct lattice



Cubic *I* reciprocal lattice unit cell of a cubic *F* direct lattice

The Reciprocal Lattice

- d-spacing of lattice planes

$$\mathbf{d}^*_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$$

$$\mathbf{d}^*_{hkl} \cdot \mathbf{d}^*_{hkl} = \frac{1}{d^2_{hkl}} = (h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*) \cdot (h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*)$$

for orthorombic, tetragonal, cubic: $\mathbf{a}^* \cdot \mathbf{b}^* = 0$

therefore:
$$\frac{1}{d^2_{hkl}} = h\mathbf{a}^* \cdot h\mathbf{a}^* + k\mathbf{b}^* \cdot k\mathbf{b}^* + l\mathbf{c}^* \cdot l\mathbf{c}^* = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

$$\left(\mathbf{a}^* \cdot \mathbf{a}^* = \frac{1}{a^2} \right)$$

- Angle ρ between plane normals $(h_1 k_1 l_1)$ and $(h_2 k_2 l_2)$

the angle between two vectors is $\cos\rho = \frac{\mathbf{a} \cdot \mathbf{b}}{ab}$

therefore: $\cos\rho = \frac{\mathbf{d}^*_{h_1 k_1 l_1} \cdot \mathbf{d}^*_{h_2 k_2 l_2}}{\left|\mathbf{d}^*_{h_1 k_1 l_1}\right| \left|\mathbf{d}^*_{h_2 k_2 l_2}\right|}$

Slip and Twining

Where from loads / forces?

1. During service

    - Structure, machine, tool, etc

2. During processing

    - forging, rolling, casting, welding etc

What are the happenings?

1. No change in shape
2. Change in shape
3. Breaking into pieces

The happenings in terms of mechanics

1. No deformation / minute elastic deformation
2. Excessive elastic deformation
3. Yielding / Plastic deformation
4. Fracture

} Failure

Are they desirable?

1. No deformation : Structural applications
2. Elastic deformation: Springs
3. Plastic deformation : Metal working applications
   Strengthening
4. Plastic deformation + Fracture : Machining, Testing

Slip Systems

- **Preferred planes for dislocation movement (slip planes)**
  Preferred crystallographic directions (slip directions)
  Slip planes + directions (slip systems)
- **More no. of slip systems indicates that material is ductile**
- **Normally No. of slip systems > 5 termed as ductile materials**
- **Most of BCC materials are ductile in nature**

Mechanisms of plastic deformation in metals - Slip

•Two prominent mechanisms of plastic deformation, namely ***slip and twinning*** **.**

•Slip is the prominent mechanism of plastic deformation in metals. It involves sliding of blocks of crystal over one other along definite crystallographic planes, called slip planes.

•It is analogous to a deck of cards when it is pushed from one end. Slip occurs when shear stress applied exceeds a critical value.

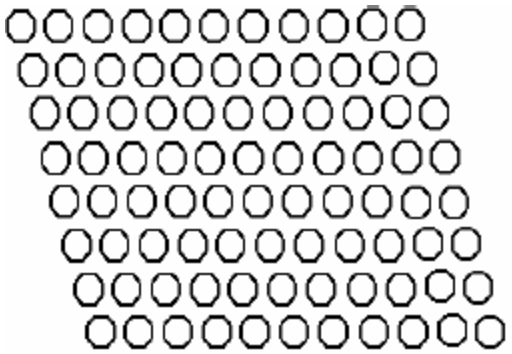
Mechanisms of plastic deformation in metals – Twinning

Twinning

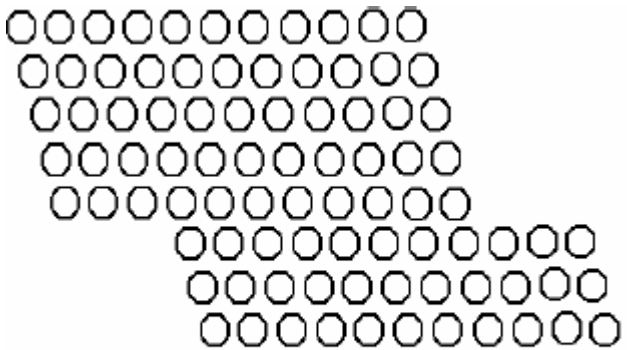
•Portion of crystal takes up an orientation that is related to the orientation of the rest of the untwined lattice in a definite, symmetrical way.

•The twinned portion of the crystal is a mirror image of the parent crystal.

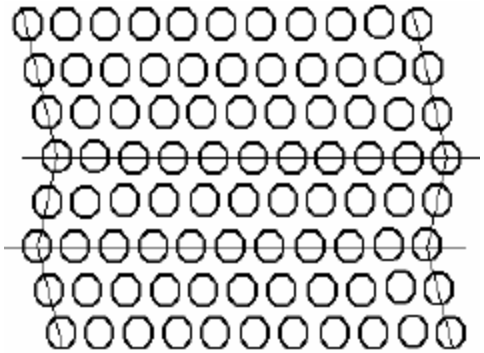
•The plane of symmetry is called twinning plane.



Undeformed Crystal



After Slip



After Twinning

Slip in Single Crystals - Resolving the Applied Stress onto the Slip System

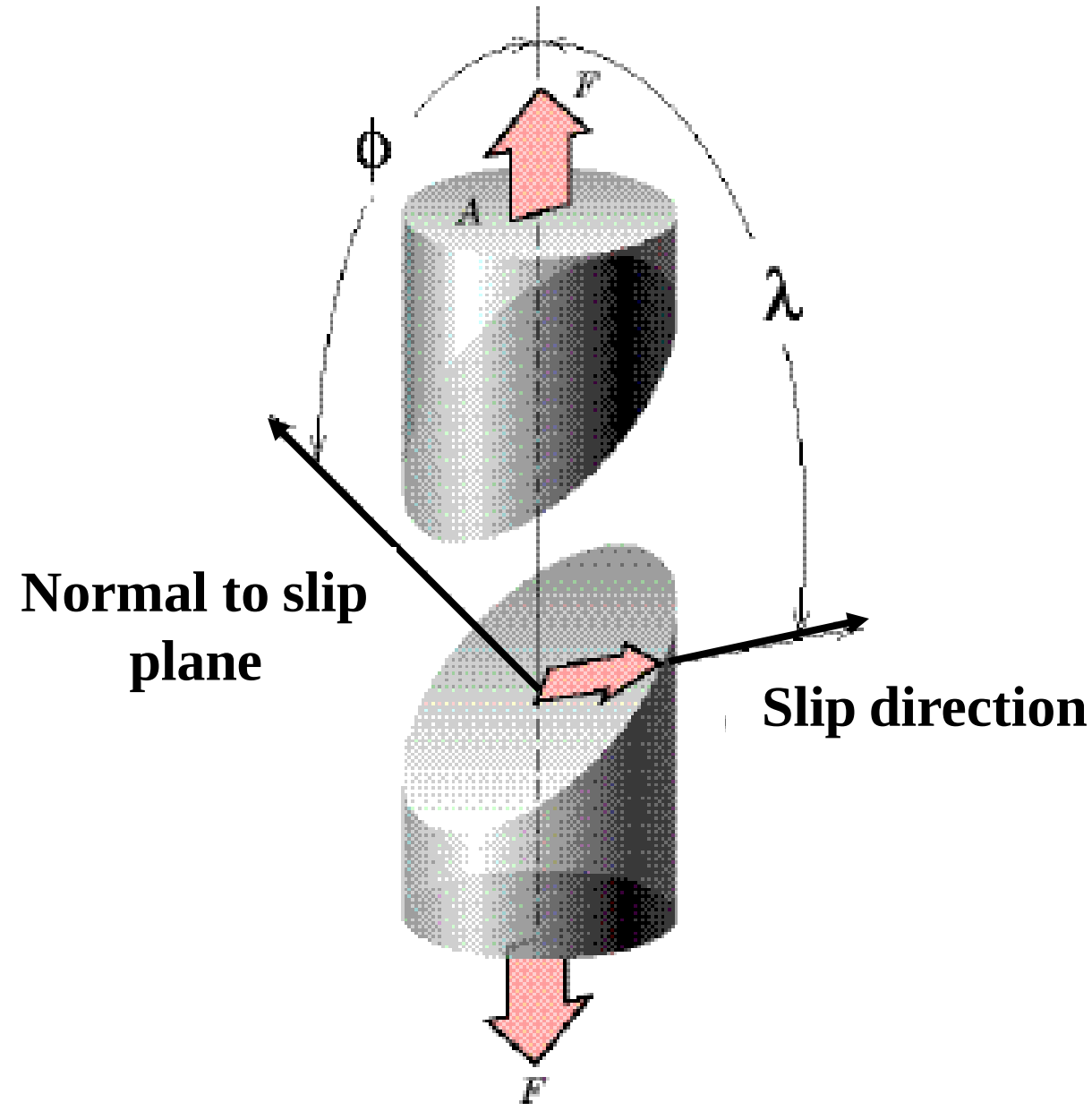
Dislocations move in particular slip system in response to shear stresses applied

Applied stress is resolved onto the slip systems

Resolved shear stress (τ_R)

- which is required to produce a plastic deformation
- it result from application of a simple tensile stress, σ

Critical Resolved shear stress (τ_{CRSS})

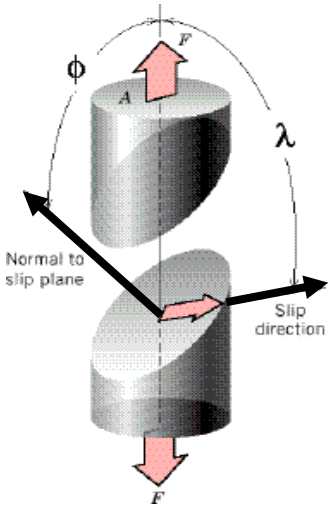

F
ϕ
A
λ
Normal to slip plane
Slip direction
F

Area of the slip plane = A / Cos ϕ

Load acting on the slip plane = P Cos λ

Resolved Shear stress = P Cos λ / A / Cos ϕ

= P / A . Cos λ Cos ϕ



$$\tau_R = \sigma \cos\phi \cos\lambda$$

Schmid law

$$\tau_R / \sigma = \text{Cos } \lambda \quad \text{Cos } \phi = M$$

M = Schmid factor

$$\tau_{CRSS} = \sigma_y (\cos\phi \cos\lambda)_{MAX}$$

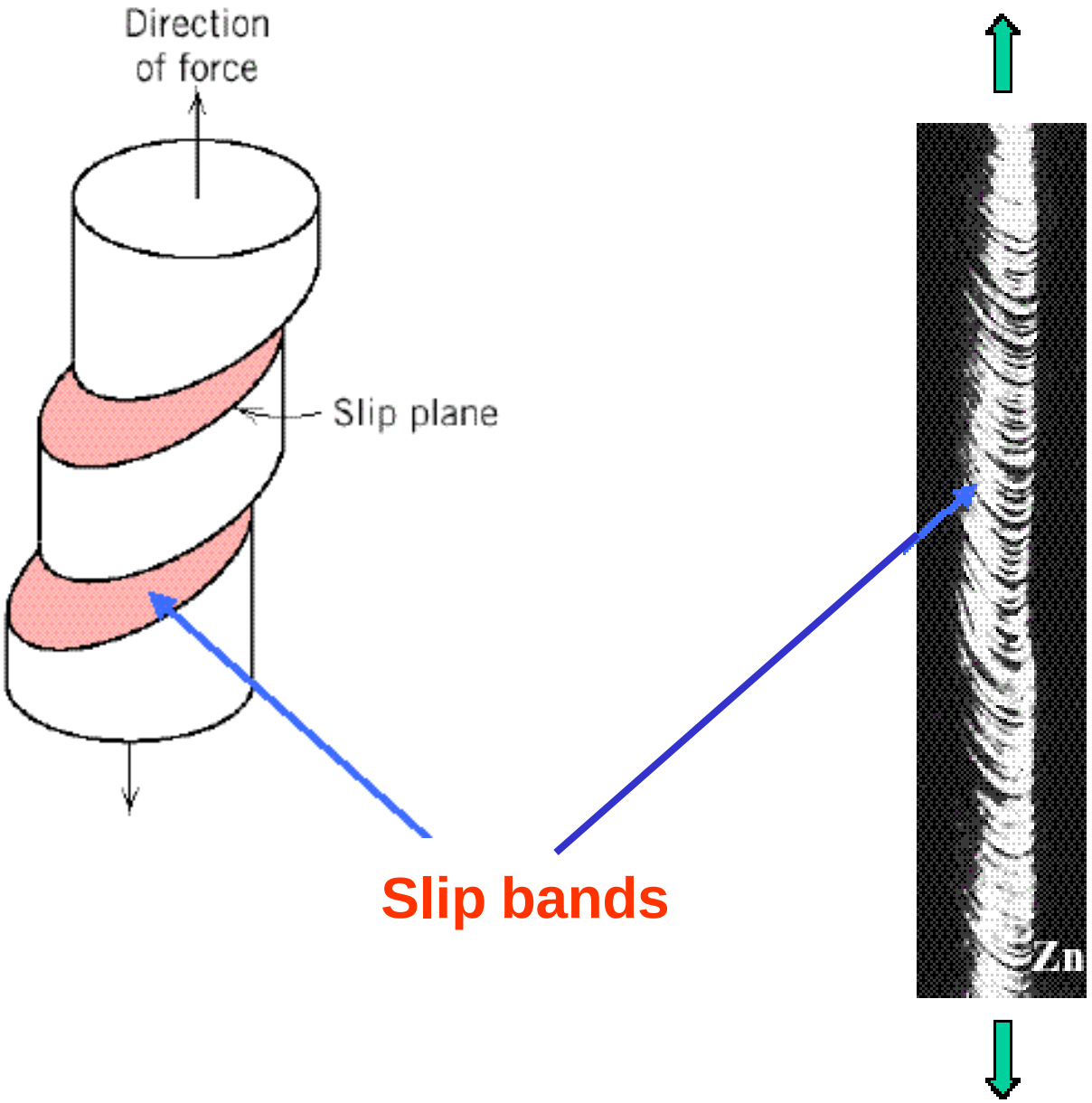
$$\sigma_y = \frac{\tau_{CRSS}}{(\cos\phi \cos\lambda)_{MAX}}$$

Maximum value of (M = cosϕ cosλ) corresponds to $\phi = \lambda = 45^o$, M = 0.5, $\sigma_y = 2\ \tau_{CRSS}$

Slip will occur first in slip systems oriented close to this angle ($\phi = \lambda = 45^o$) w.r.t the applied stress

This mainly depends on composition and temperature

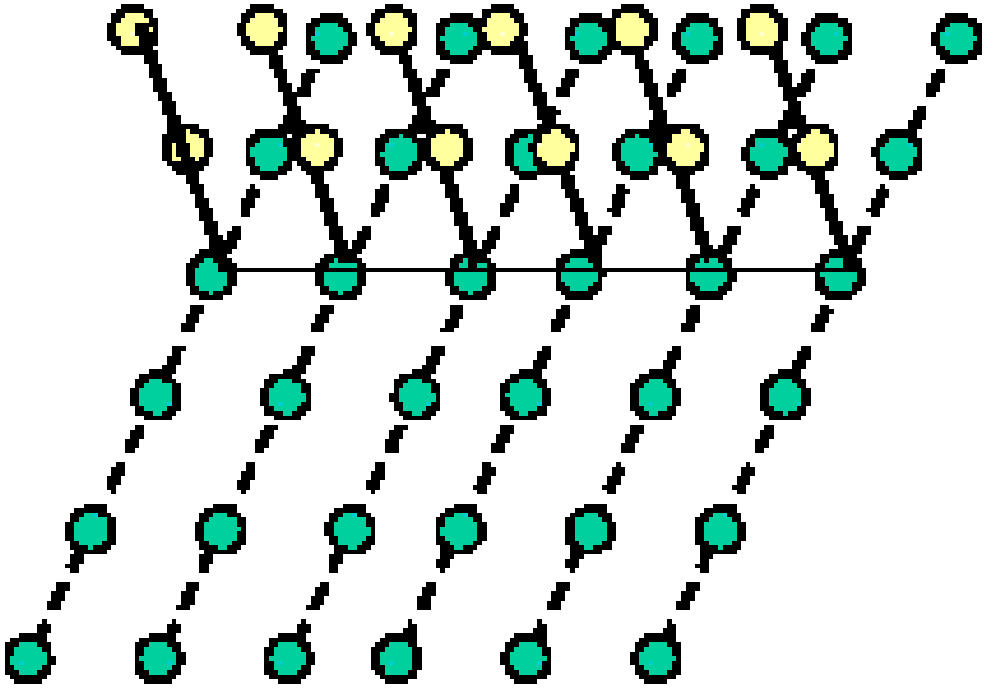
Slip in a Single Crystal

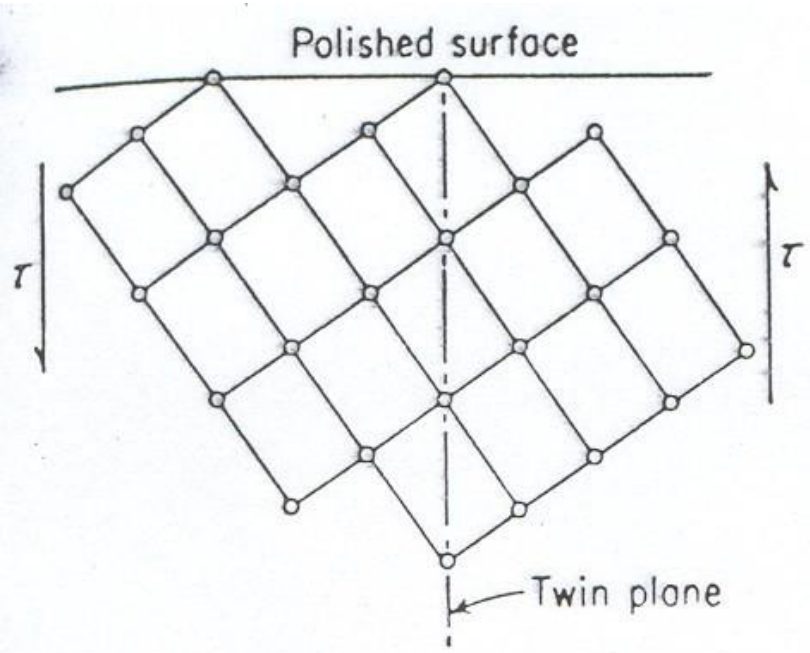


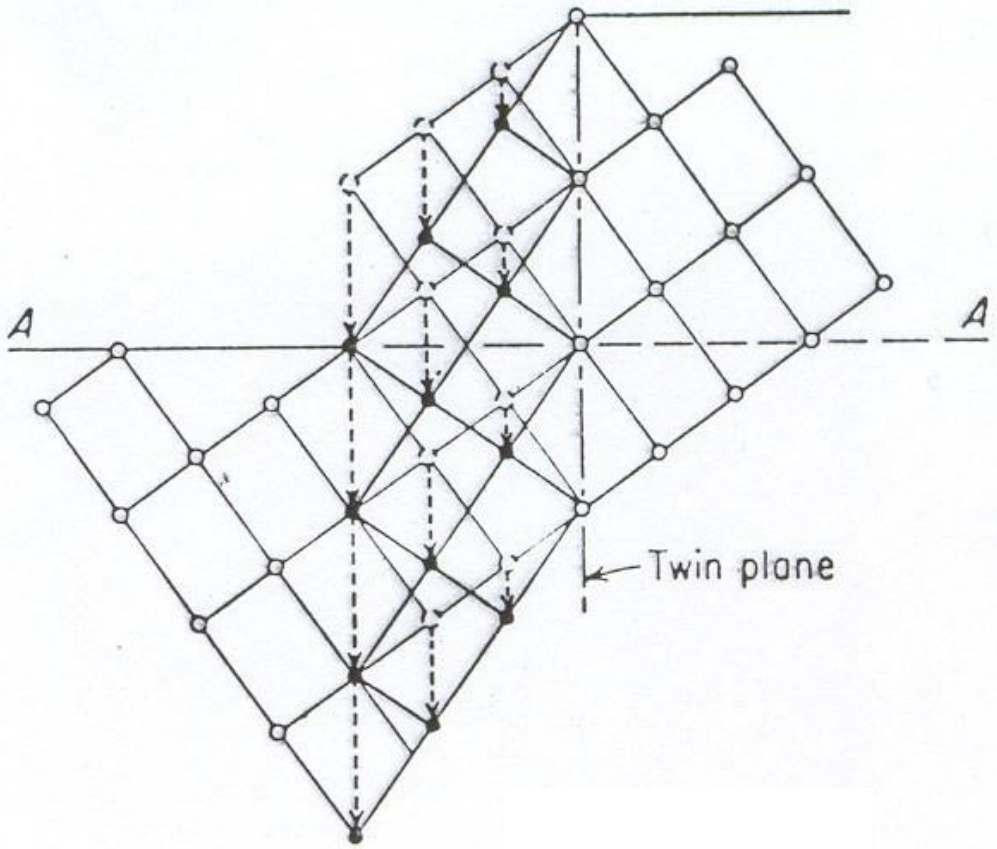
Deformation by Twinning

- **Whenever slip is not possible**

- **Creates a deformed portion grain which is just mirror image of the rest of the parent grain**




Polished surface
τ
τ
Twin plane


A
A
Twin plane

Twin Types

- **Mechanical twins** - **BCC and HCP**
- **Annealing twins** - **FCC**

Slip Vs Twinning

Slip	Twin
Orientation across the slip plane is same	Orientation across the twin plane is different
Atomic movements are equal to atomic distances	Atomic movements are lesser than atomic distances
Atoms are moving in only one plane (slip plane)	Atoms are moving in all planes in the region of twin
Takes place in milli seconds	Takes place in less than micro seconds
Takes place at low strain rates	Takes place at high strain rates
No sound is created	A click sound (Tin cry)