chem 5390

Advanced X-ray Analysis

LECTURE 4

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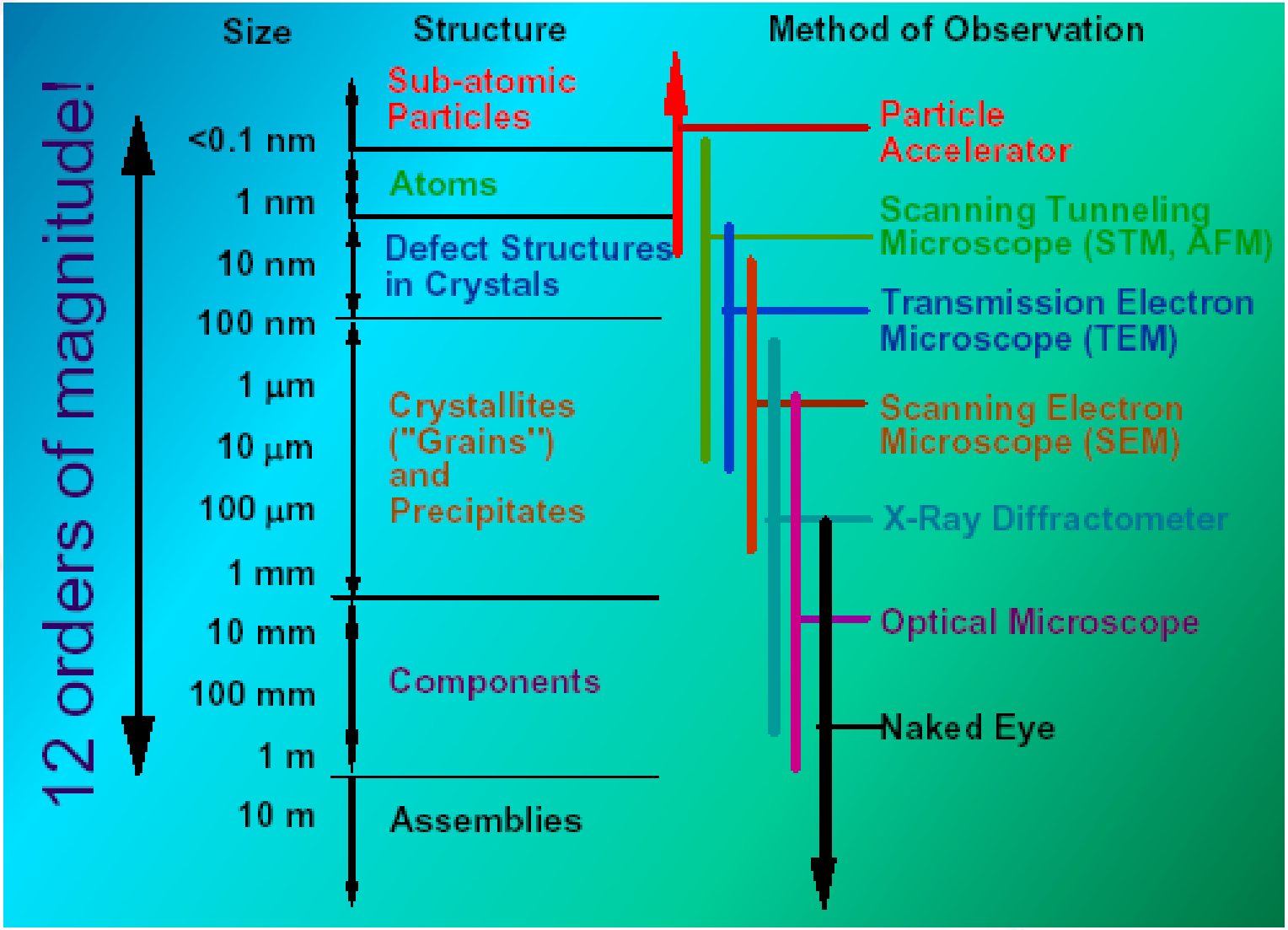
Crystallography



Crystallography

For electromagnetic radiation to be diffracted the spacing in the grating should be of the same order as the wavelength

In crystals the typical interatomic spacing ~ 2-3 Å so the suitable radiation is X-rays

Hence, x-rays can be used for the study of crystal structures

Crystallography

A beam of X-rays directed at a crystal interacts with the electrons of the atoms in the crystal

The electrons oscillate under the influence of the incoming x-rays and become secondary sources of EM radiation

The secondary radiation is in all directions

The waves emitted by the electrons have the same frequency as the incoming x-rays → coherent

The emission will undergo constructive or destructive interference

Crystallography

Many θs (orientations)
Powder specimen

POWDER METHOD

$\lambda \rightarrow$ fixed
$\theta \rightarrow$ variable

Single θ

LAUE TECHNIQUE

$\lambda \rightarrow$ variable
$\theta \rightarrow$ fixed

θ Varied by rotation

ROTATING CRYSTAL METHOD

$\lambda \rightarrow$ fixed
$\theta \rightarrow$ rotated

Crystallography

Geometry and the structure of crystals

A. Lattices

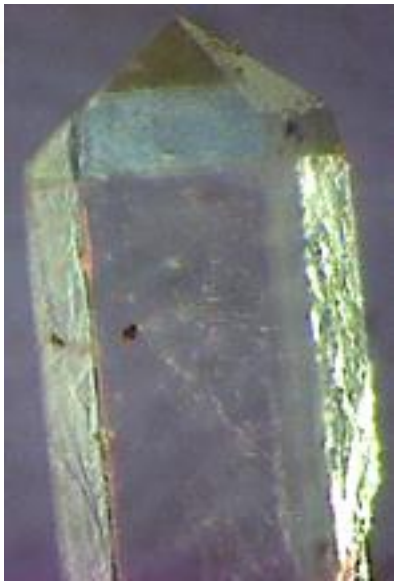
Solids can be generally classified as: single crystal, polycrystalline, or amorphous.

Crystallography

Geometry and the structure of crystals

A. Lattices

<u>Crystal</u> - solid composed of atoms arranged in a pattern periodic in three dimensions. (long-range order)



Crystallography

Geometry and the structure of crystals

A. Lattices

<u>Polycrystals</u> – consist of many single-crystal regions (grains) separated by grain boundaries.

Crystallography

Geometry and the structure of crystals

A. Lattices

<u>Amorphous</u> – consist of only short range order. (glass, polymers)

Crystallography

Many common inorganic materials are usually crystalline:

- **Metals: Cu, Zn, Fe, Cu-Zn alloys**
- **Semiconductors: Si, Ge, GaAs**
- **Ceramics: Alumina (Al_2O_3), Zirconia (Zr_2O_3), SiC**

Also, the usual form of crystalline materials (i.e. Cu wire or a piece of alumina) is polycrystalline and special care has to be taken to produce single crystals

Polymeric materials are can range from amorphous to semi-crystalline

The crystal structure directly influences the properties of the material

Crystallography

Ideal Crystals → Real Crystals → Microstructures → Material → Component

Ideal Crystal
(Considers ***both*** Geometrical Entity AND Physical Property/)

Crystal*
(Here we consider ***either*** geometrical entity OR physical property)

Crystal**
(Consider ***either*** the Orientational OR the Positional Order)

'Real Crystal'
(Presence of Crystalline defects & Free Surface & Thermal Vibration)

~Microconstituents
(Put in Multiple Crystals *(Phases)* giving rise to interfacial defects)

Microstructure
(Put in multiple ~microconstituents and add additional residual stress†)

Material
(Put in many microstructures)

Component
(Put in material/s and/or material treatment i.e. temperature/pressure)

Crystallography

Geometry and the structure of crystals

Consider two definitions of a crystal:

1) Crystal = Lattice + Motif (Basis)

2) Crystal = Space Group + Asymmetric unit (+Wyckoff positions).

The second definition is the more advanced one but the first definition can be more practical.

Initially we may start with ideal mathematical crystals and then slowly relax various conditions to get into practical crystals.

Crystallography

Geometry and the structure of crystals

Motif or Basis: an entity (typically an atom or a group of atoms) associated with each lattice point

Lattice ➢ the underlying periodicity of the crystal

Motif ➢ Entity associated with each lattice points

Lattice ➢ how to repeat

Motif ➢ what to repeat

Lattice

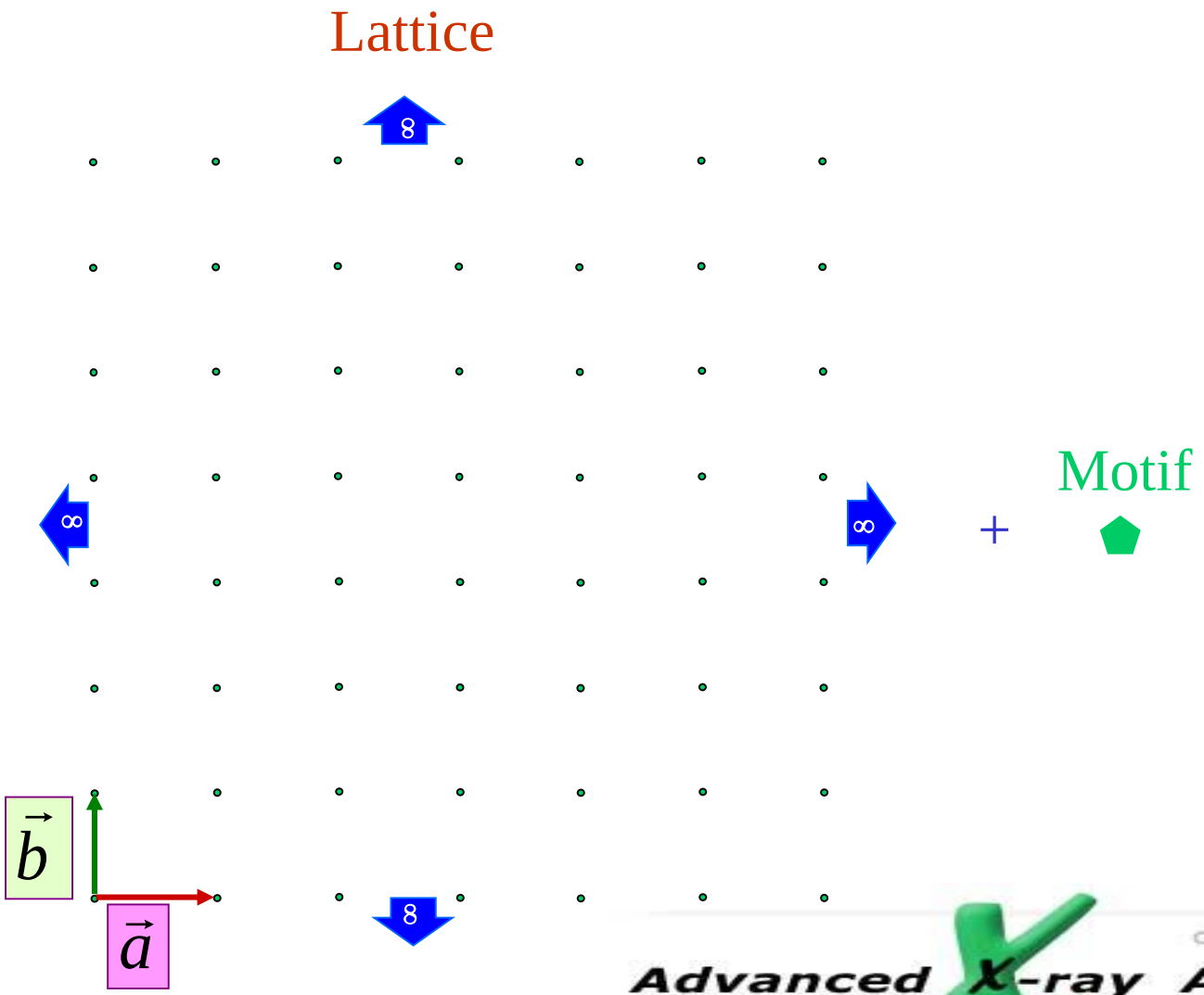
Translationally periodic arrangement of points

Crystal

Translationally periodic arrangement of motifs (basis)

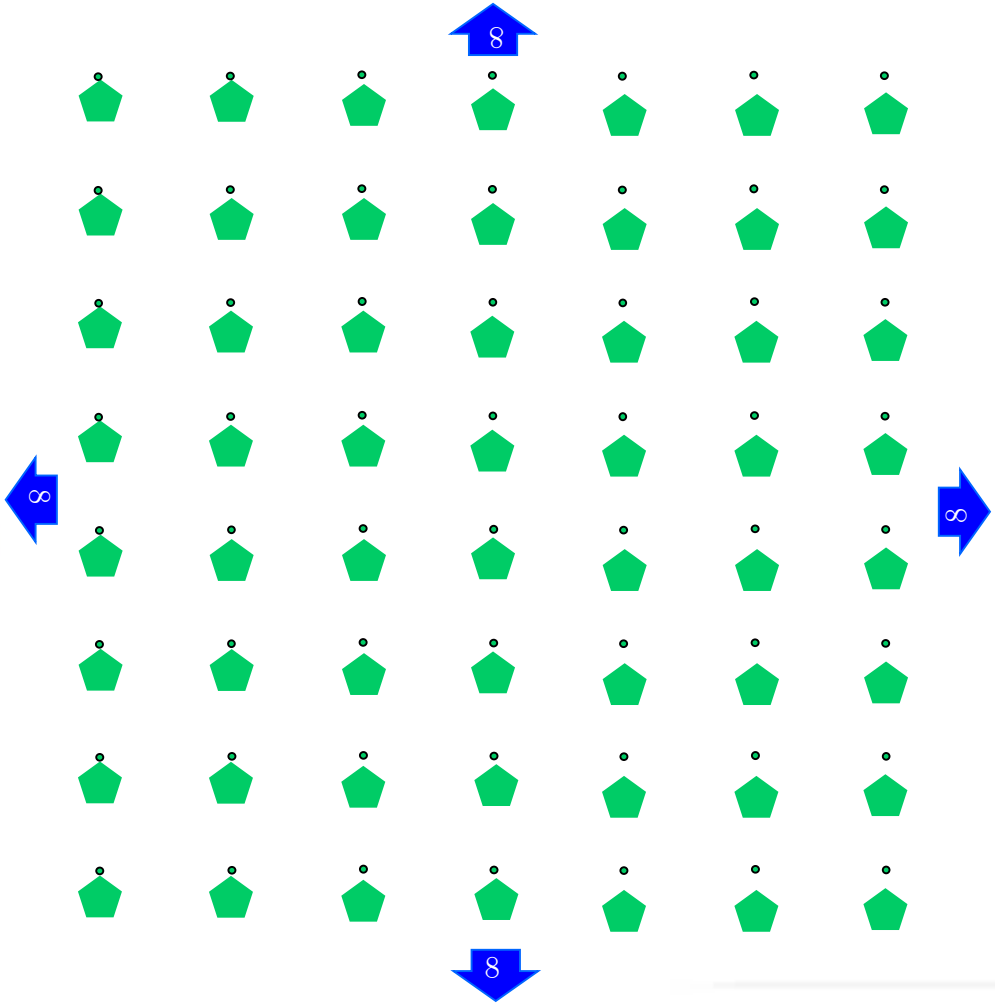
Crystallography

Geometry and the structure of crystals



Crystallography

Geometry and the structure of crystals



Crystallography

Geometry and the structure of crystals

Three-dimensional motif/basis (groups of atoms or molecules) is the “core” repeated unit

The motif/basis is repeated in space by movement operations – translation, rotation and reflection

Crystal structures are “created” in a two-step process:

Point-group operations create the motif/basis

Translation operation produce the crystal structure

Crystallography

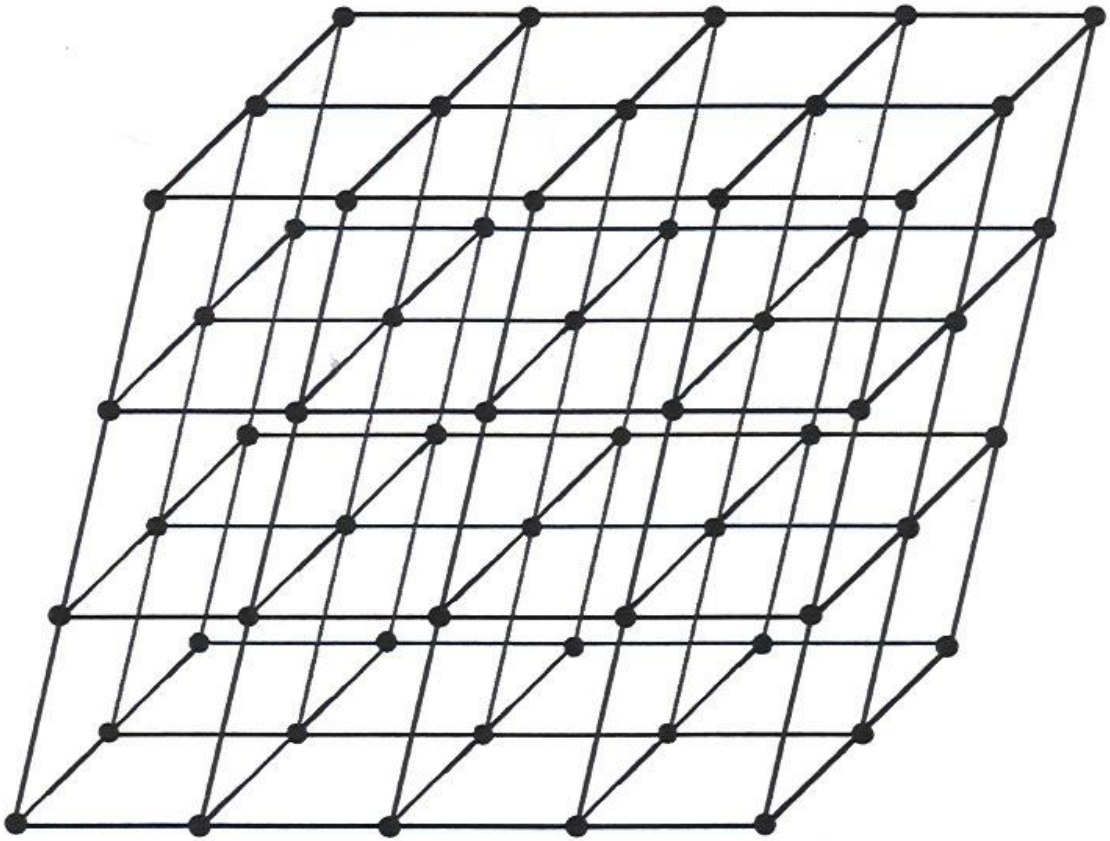
Geometry and the structure of crystals

A. Lattices

Crystal - solid composed of atoms arranged in a pattern periodic in three dimensions.

Point lattice - an array of points in space so arranged that each point has identical surroundings.

Since all points are identical we can choose a repeating group to represent a unit cell.



A Point Lattice.

Crystallography

Geometry and the structure of crystals

A. Lattices

Lattice is "an imaginary pattern of points in which every point has an environment that is identical to that of any other point in the pattern.

The lattice must be described in terms of 3-dimensional coordinates related to the translation directions:

Lattice points, Miller indices, Lattice planes (and the "d-spacings" between them) are conventions that facilitate description of the lattice.

Although it is an imaginary construct, the lattice is used to describe the structure of real materials.

Crystallography

Geometry and the structure of crystals

A. Lattices

Point lattices are used out of convenience, to allow one to focus on the geometry of periodic arrays and ignore actual atoms, ions, or molecules. The crystal is substituted with a lattice (3-D array of points).

Crystallography

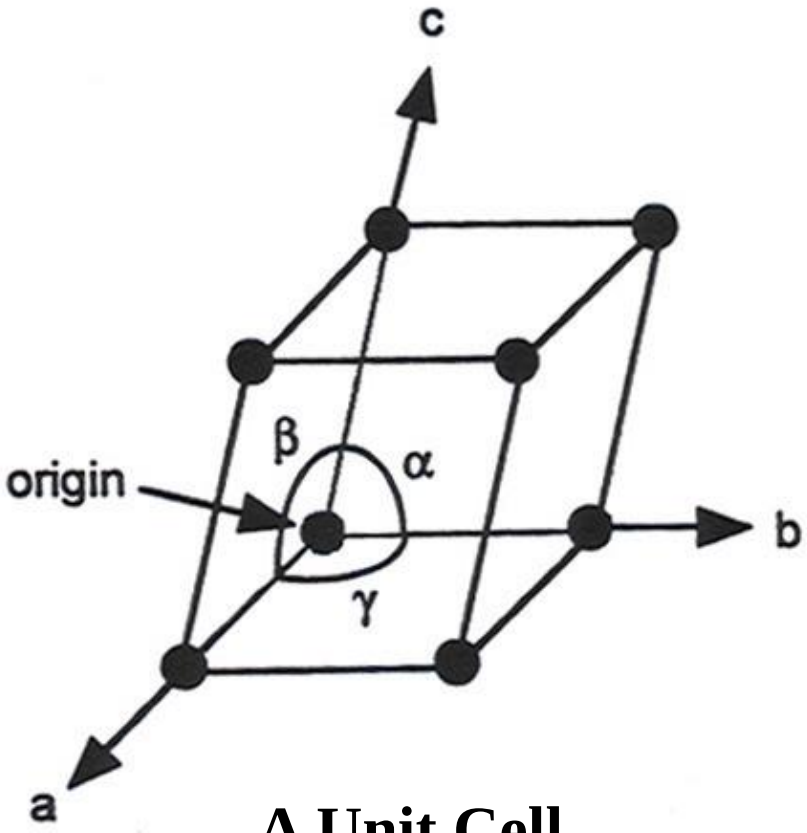
A. Lattices

The size and shape of the unit cell can be described by three vectors, a, b, and c (called the crystallographic axes of the cell).

The unit cell can also be described in terms of lengths (a, b, c) and the angles between them (α, β, γ).

The lengths and angles are the lattice constants or lattice parameters of the unit cell.

Notice that the entire point lattice can be built by translating the unit cell.



A Unit Cell.

Axis	**a**	**b**	**c**
Lattice Parameters:			
Lengths	a	b	c
Inter-axial angle	α	β	γ

Crystallography

B. Crystal Systems

Unit cells can be produced in various shapes

Example: if the planes in the three sets are all equally spaced and perpendicular to each other, the unit cell is cubic.

a =b = c $\alpha = \beta = \gamma = 90^{o}$

Crystallography

B. Crystal Systems

- Crystals can have a wide range of lattice parameter sizes ranging from
  - Small unit cells (a_{Cu} (FCC)= 3.61 Å)

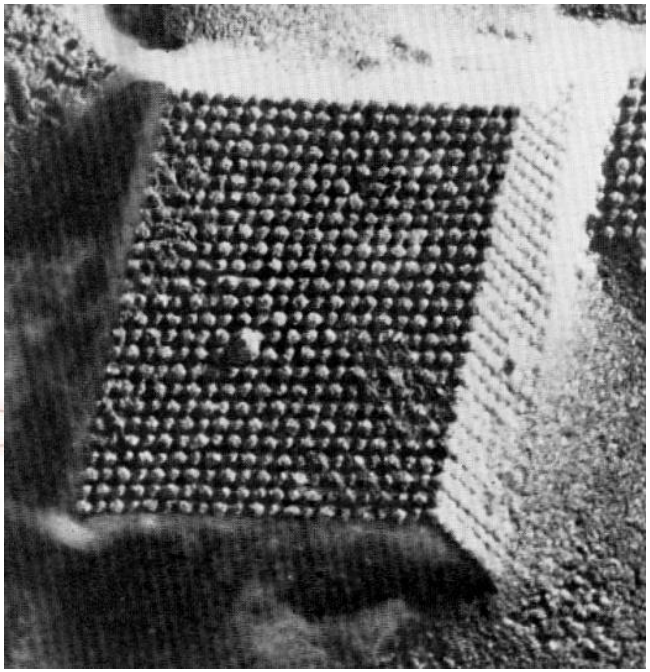
  to
  - Medium sized UC ($a_{Fullerene}$ (FCC)= 14.17 Å)

  to
  - Large unit cells ($a_{CPV\ virus*}$ (BCC) = 103.7 Å)

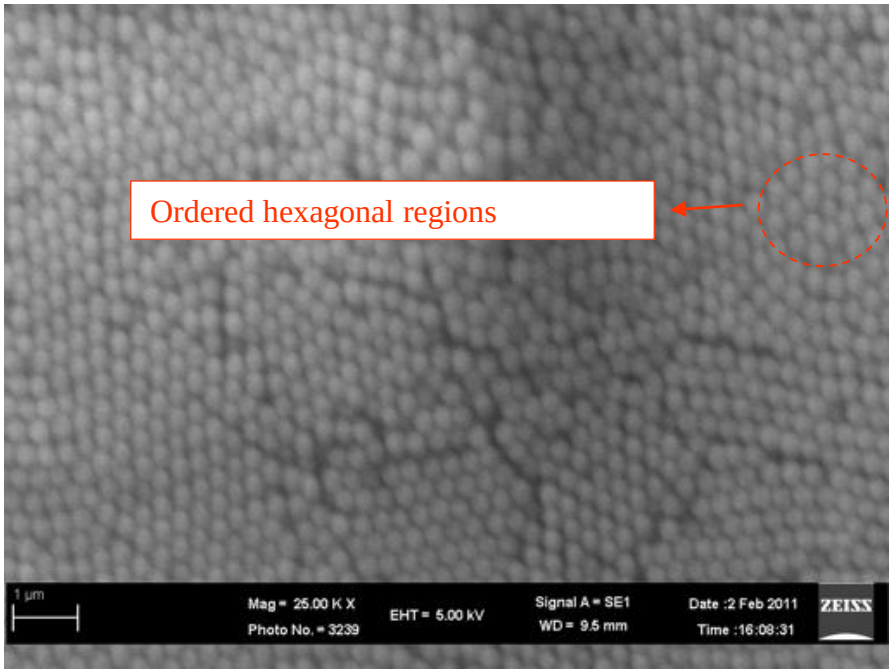
- Typically colloidal and organic crystals have large unit cells
- An example of colloidal crystal is silica nanospheres forming a 2D crystal with 4-fold symmetry.

Crystallography

B. Crystal Systems



2D parallelogram crystal of Tobacco Mosaic Virus



Monolayer of SiO_2 nanoparticles (Glass spheres of diameter: ~350 nm) forming crystalline regions

(Note: sample is only partly crystalline).

Crystallography

B. Crystal Systems

It turns out that only seven different kinds of cells are necessary to include all the possible point lattices - called <u>Crystal Systems.</u>

Arranged in order of increasing symmetry,
triclinic – lowest symmetry **cubic – highest symmetry**

What are the symmetries of the 7 crystal systems?

	Characteristic symmetry
Cubic	Four 3-fold rotation axes *(two will generate the other two)*
Hexagonal	One 6-fold rotation axis (or roto-inversion axis)
Tetragonal	(Only) One 4-fold rotation axis (or roto-inversion axis)
Trigonal	(Only) One 3-fold rotation axis (or roto-inversion axis)
Orthorhombic	(Only) Three $\perp$ 2-fold rotation axes (or roto-inversion axis)
Monoclinic	(Only) One 2-fold rotation axis (or roto-inversion axis)
Triclinic	None

(The symbol $\neq$ means that equality is not required by symmetry. Accidental equality may occur, as shown by an example in Sec. 2–4.)

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

* Also called trigonal.

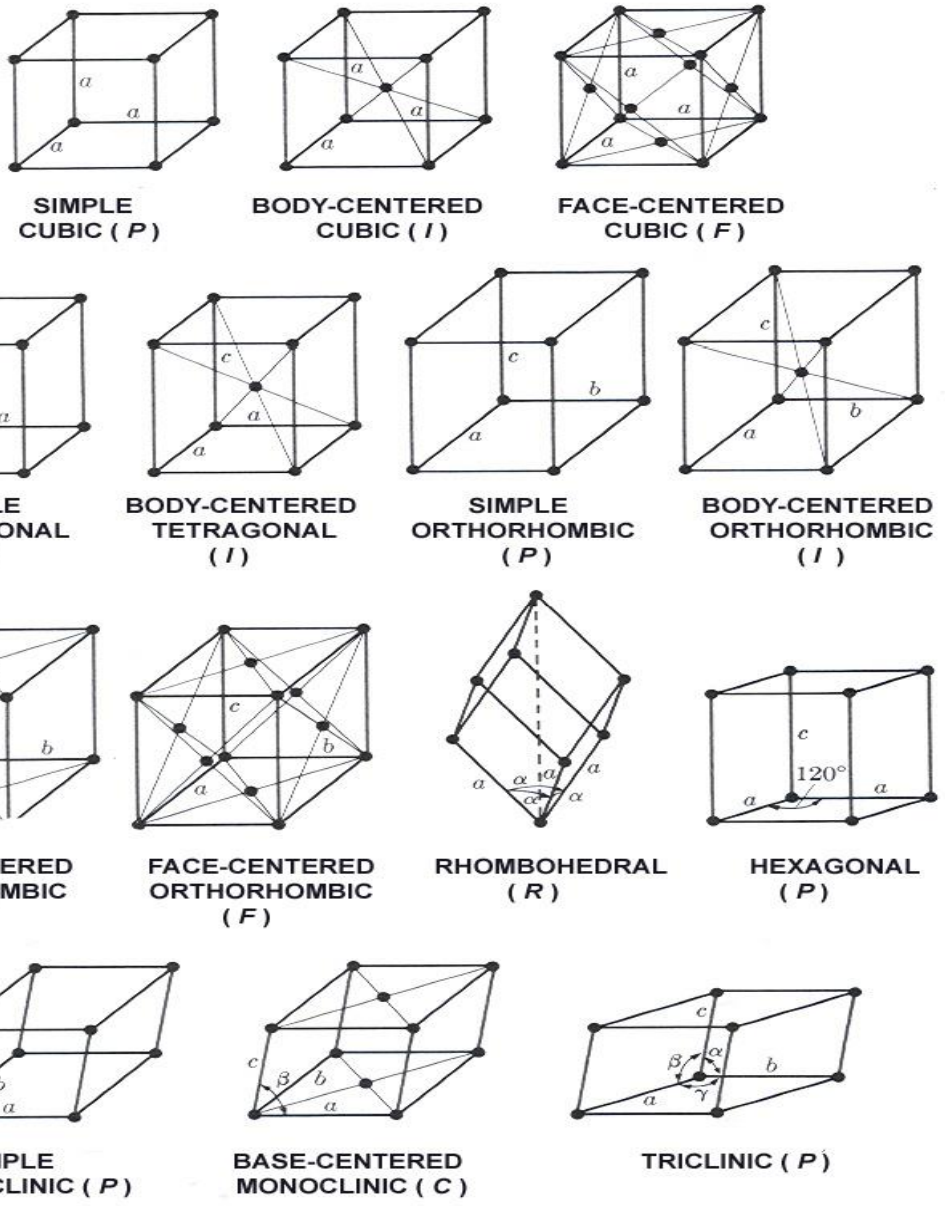
Crystal systems and Bravais lattices.

Crystallography

Geometry and the structure of crystals

B. Crystal Systems

Within the crystal systems, there are 14 possible point lattices called Bravais lattices or point lattices (discovered by Bravais in 1848).



The fourteen Bravais lattices.

Crystallography

B. Crystal Systems

Primitive (or simple) cells - have only one lattice point per cell. Symbol P or R

Nonprimitive cells - have more than one lattice point per cell. Symbols I, F, or C

Example:

A cell having points on only the corners is primitive. A cell with points on corners and in the interior or on the faces is non-primitive.

Crystallography

B. Crystal Systems

P - primitive - lattice point on each corner.

F - face-centered - lattice point at each face plus corners.

I - body-centered - lattice point at center of cell plus corners.

R - rhombohedral - primitive.

Crystallography

B. Crystal Systems

Number of lattice points per cell is:

$N = Ni + Nf/2 + Nc/8$

Ni - number of interior points.

Nf - number of points on faces (shared).

Nc - number of points on corners (shared).

Crystallography

B. Crystal Systems

Example:

For a cubic P, what is N? (number of lattice points per cell)

N = Ni + Nf/2 + Nc/8 = 0 + 0 + 8/8 = 1

For cubic I, what is N?

N = 1 + 0 + 8/8 = 2

For cubic F, what is N?

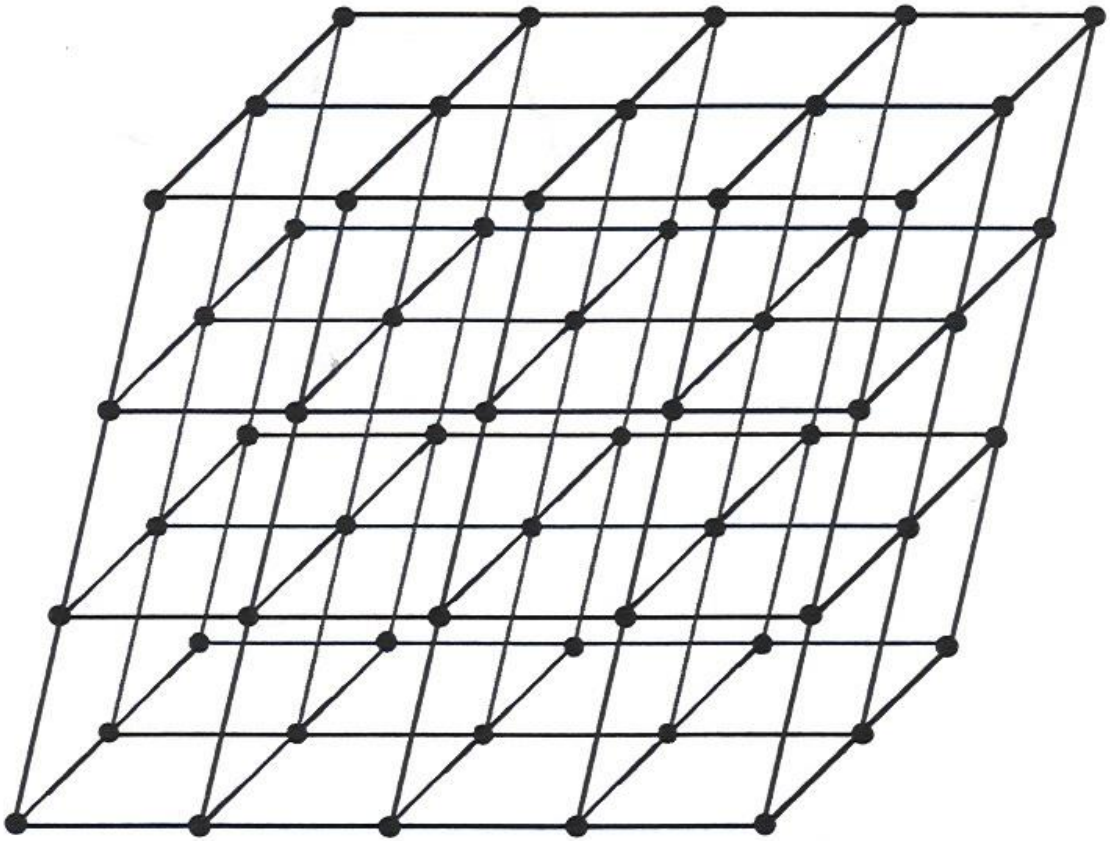
N = 0 + 6/2 + 8/8 = 4

Crystallography

B. Crystal Systems

So how do we relate lattice points to atoms?

In a crystal - a lattice point may be occupied by one atom or by a group of atoms.



A Point Lattice.

Crystallography

B. Crystal Systems

1. Symmetry

Both Bravais lattices and real crystals exhibit various kinds of symmetry. This symmetry is represented by symmetry operations.

These include:

- **reflection**
- **rotation**
- **inversion**
- **rotation-inversion**

Crystallography

Geometry and the structure of crystals

Symmetry Element	Operation	
	Herman-Mauguin (Cystallographic)	Schonflies (Spectroscopy)
Mirror Plane	m	σ_v, σ_h
Rotation axis	n (=2, 3, 4, or 6)	C_n (C_2, C_3, etc)
Center of symmetry	$\bar{1}$	i

Crystallography

Geometry and the structure of crystals

Symmetry Element	Operation	
	Written Symbol	Graphic
Mirror Plane	m	------
Rotation axis	2	
	3	▲
	4	◆
	6	
Improper	$\bar{1}$	none
	2bar=m	-------
	3bar	
	4bar	
	6bar	

Crystallography

Geometry and the structure of crystals

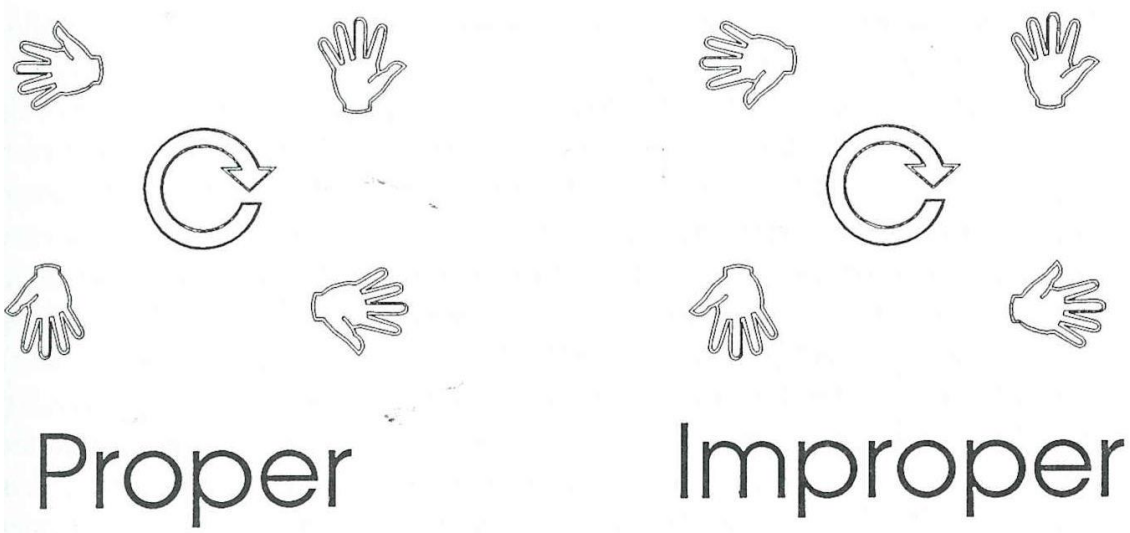


Figure 2.3. A proper and improper fourfold rotation.

Table 2.1. The Crystallographic Point Group Symmetry Elements

Degrees of Rotation $(360/n)$	Proper Axis (n)	Improper Axis $(\bar{n})$
360°	1	$\bar{1}$
180°	2	$m(=\bar{2})$
120°	3	$\bar{3}$
90°	4	$\bar{4}$
60°	6	$\bar{6}$

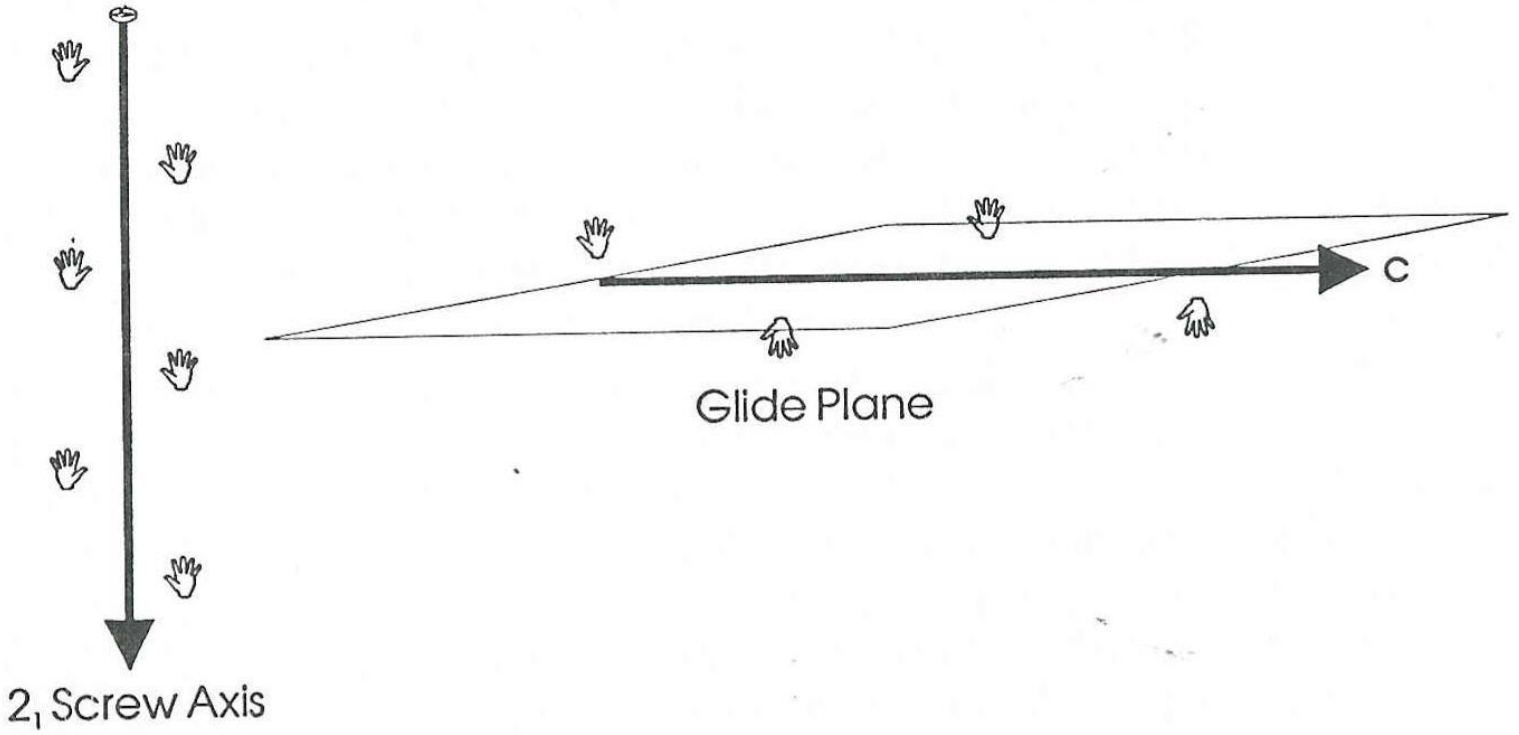
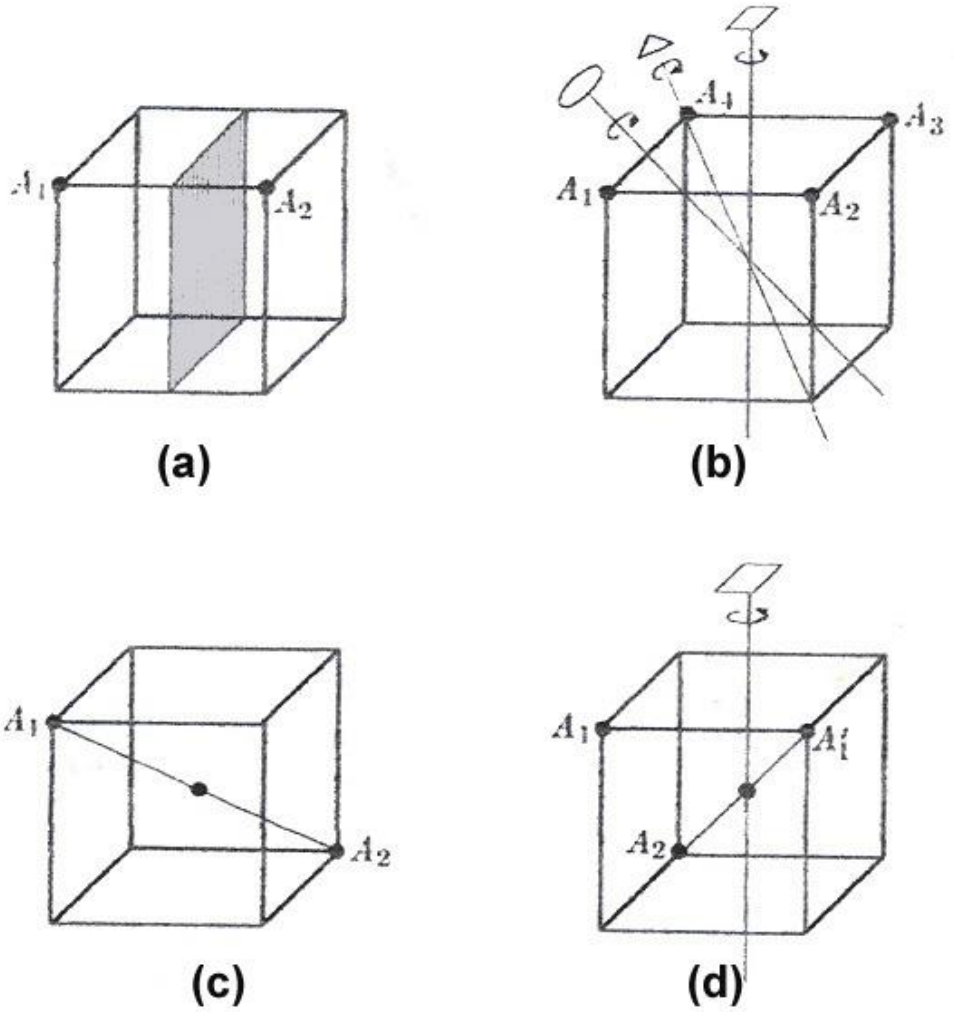


Figure 2.6. A 2_1 screw axis and a *c* glide plane.



Some symmetry elements of a cube. (a) Reflection plane. A_1 becomes A_2. (b) Rotation axes. 4-fold axis: A_1 becomes A_2; 3-fold axis: A_1 becomes A_3; 2-fold axis: A_1 becomes A_4. (c) Inversion center. A_1 becomes A_2. (d) Rotation-inversion axis. 4-fold axis: A_1 becomes A'_1; Inversion center: A'_1 becomes A_2 .

Crystallography

B. Crystal Systems

1. Symmetry

Rotation axes may be 1, 2, 3, 4, 5, or 6-fold.

(5-fold is prohibited in crystals, however the new quasi-crystals exhibit 5-fold rotation symmetry).

Crystal systems posses a certain minimum set of symmetry elements.

Crystallography

B. Crystal Systems

1. Symmetry

There are only 32 unique ways of combining symmetry elements in objects that can repeat in 3-D to fill space.

These 32 combinations are called point groups or crystal classes.

Crystallography

B. Crystal Systems

1. Symmetry

Why do we care about point groups or crystal classes if there are the 7 crystal systems?

Some crystals can be described equally well by several types of unit cells. Symmetry is then used to choose the correct unit cell. The unit cell with the maximum symmetry is chosen to describe the space lattice.

System	Minimum symmetry elements
Cubic	Four 3-fold rotation axes
Tetragonal	One 4-fold rotation (or rotation-inversion) axis
Orthorhombic	Three perpendicular 2-fold rotation (or rotation-inversion) axes
Rhombohedral	One 3-fold rotation (or rotation-inversion) axis
Hexagonal	One 6-fold rotation (or rotation-inversion) axis
Monoclinic	One 2-fold rotation (or rotation-inversion) axis
Triclinic	None

Crystallography

B. Crystal Systems

1. Symmetry

The highest symmetry crystal system is listed first (cubic) going down to the nonsymmetrical system (triclinic).

If the 32 point groups are arranged in the various patterns allowed by the 14 Bravais lattices, there are 230 unique 3-D patterns called space groups. Each crystal structure can be classified into one of the 230 space groups. (book-Burns and Glazer).

The notation needed to describe the 230 space groups is complex.

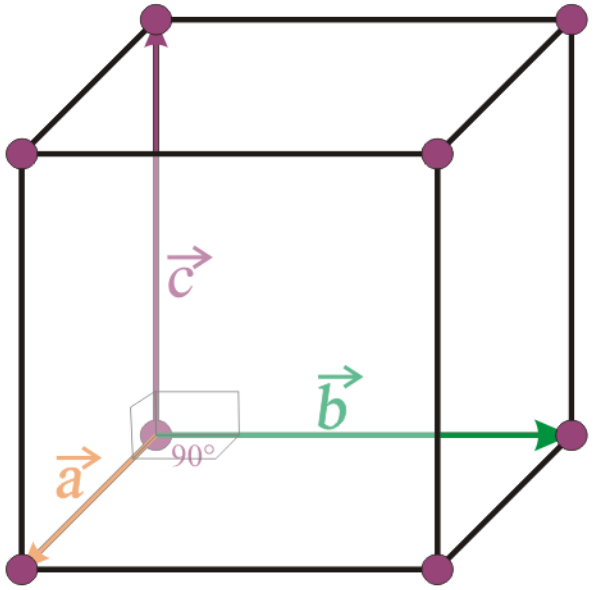
Crystallography

Cubic Crystals

$a = b = c$

$\alpha = \beta = \gamma = 90^{o}$

- Simple Cubic (P) - SC
- Body Centred Cubic (I) – BCC
- Face Centred Cubic (F) - FCC



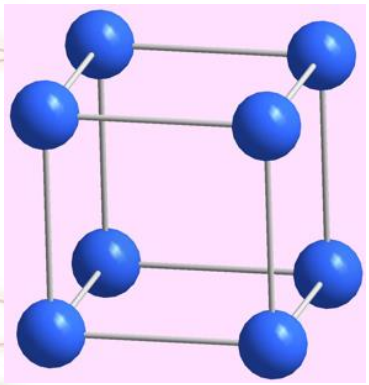
- **Elements with Cubic structure →**
  SC: F, O, Po
  BCC: Cr, Fe, Nb, K, W, V
  FCC: Al, Ar, Pb, Ni, Pd, Pt, Ge

Point groups $\Rightarrow 23,\ \bar{4}3m,\ m\bar{3},\ 432,\ \frac{4}{m}\bar{3}\frac{2}{m}$

Crystallography

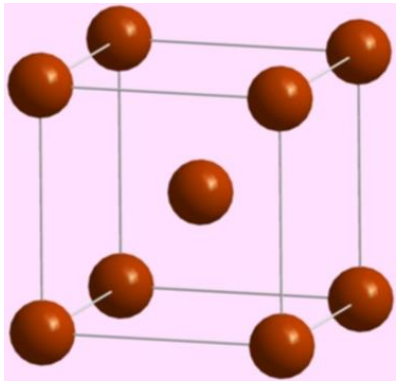
B. Crystal Systems

Examples of elements with Cubic Crystal Structure



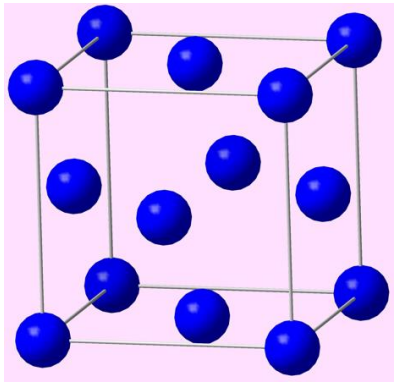
n = 1

SC



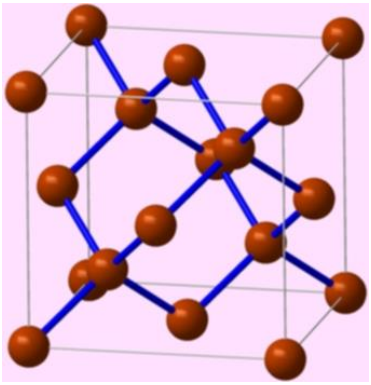
n = 2

BCC



n = 4

FCC/CCP



n = 8

DC

C (diamond)

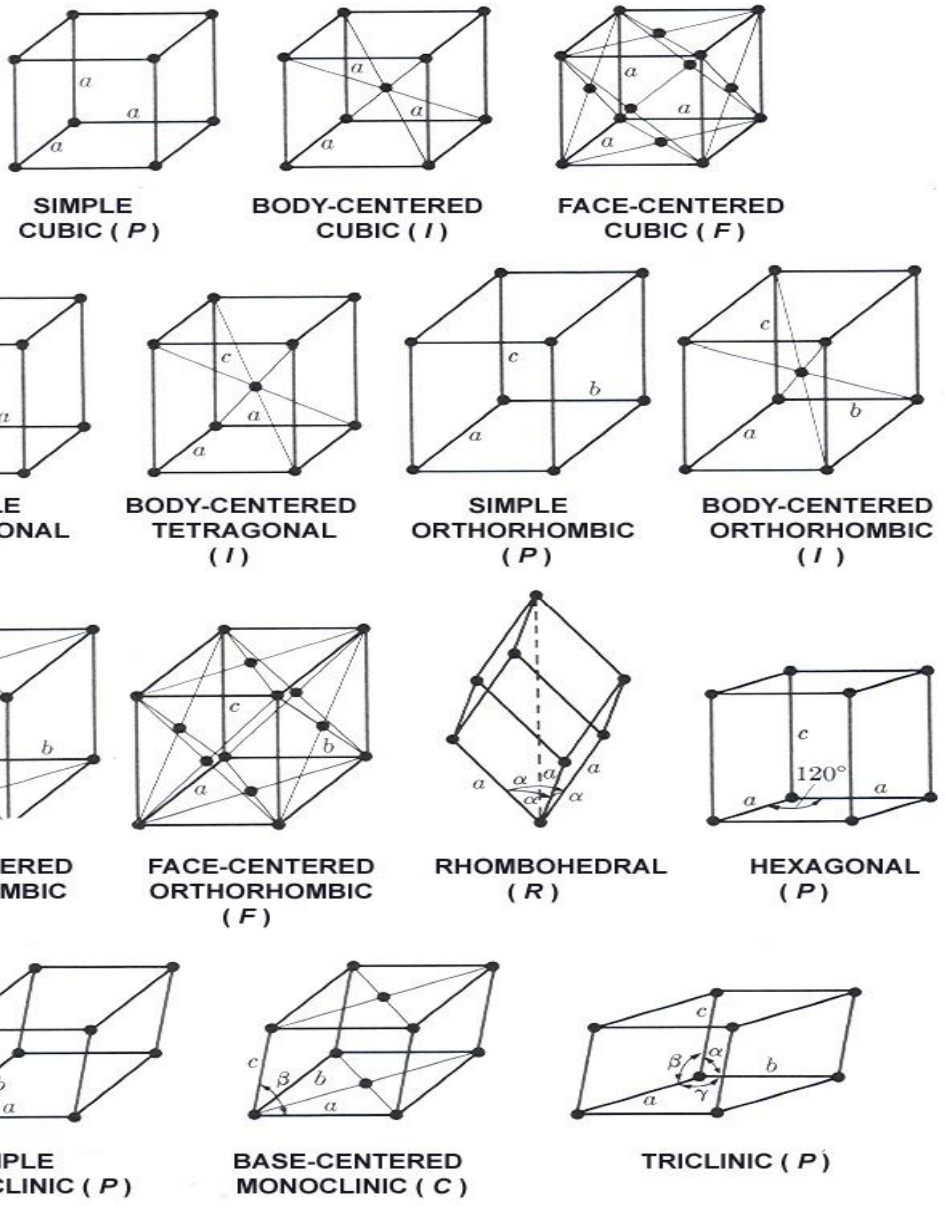
Crystallography

C. Crystal Structures

Relate Bravais lattices with actual crystal structure using a basis.

Basis - the number, composition, and arrangement of atoms for a lattice point.

Bravais lattice + basis ---> Crystal system



The fourteen Bravais lattices.

Crystallography

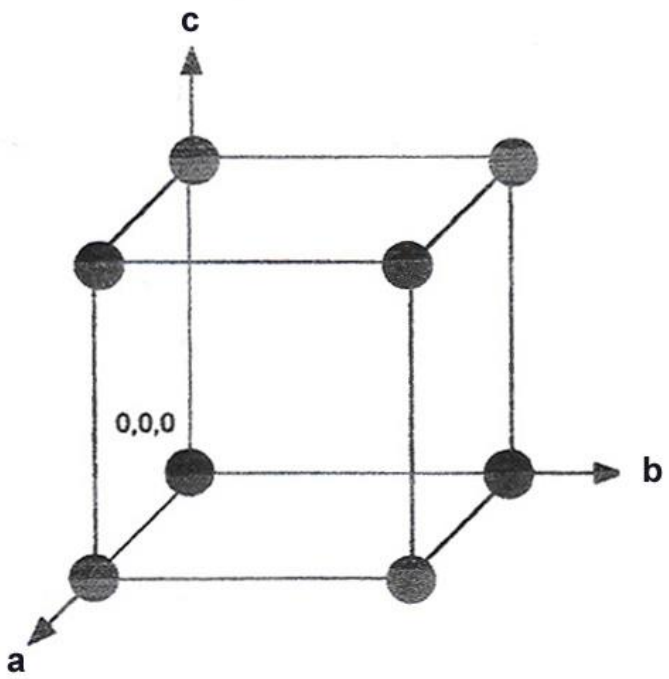
C. Crystal Structures

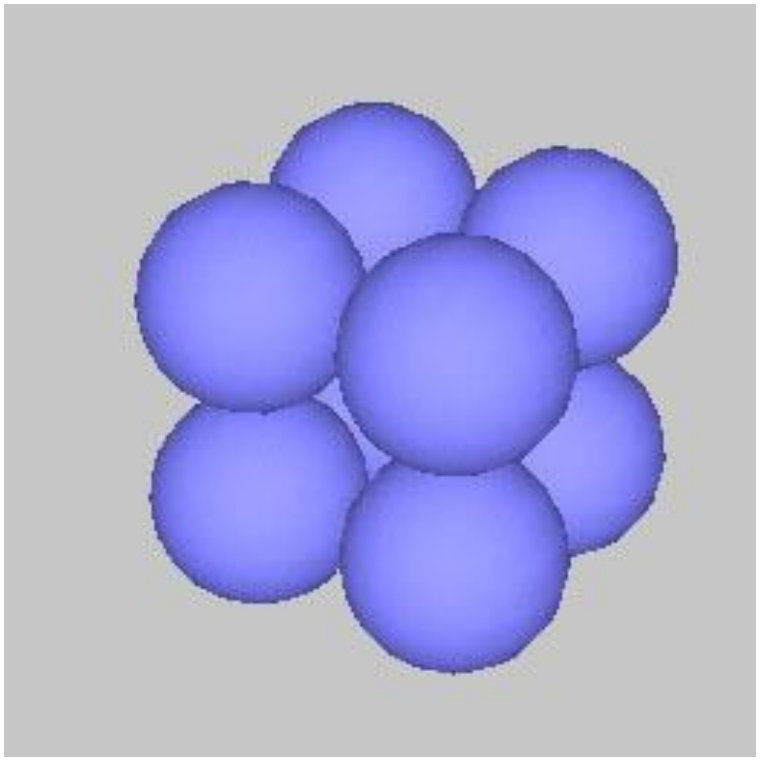
1. One atom per lattice point (basis)

Each atom is identical - start with cubic system (3 different kinds)

a. Primitive cubic

Primitive cubic (P) lattice + one atom ---> Primitive structure (or simple).





Simple cubic structure.

Crystallography

C. Crystal Structures

1. One atom per lattice point (basis)

a. Primitive cubic

To define the cell we use 0,0,0 as the coordinate. (This is the origin). If we move one full lattice parameter, then we reach the next origin of the next unit cell, so 0,0,0 is all we need to define the cell (N = 1)

This structure is rare.

Examples: Po (α-Polonium) and nonequilibrium alloys

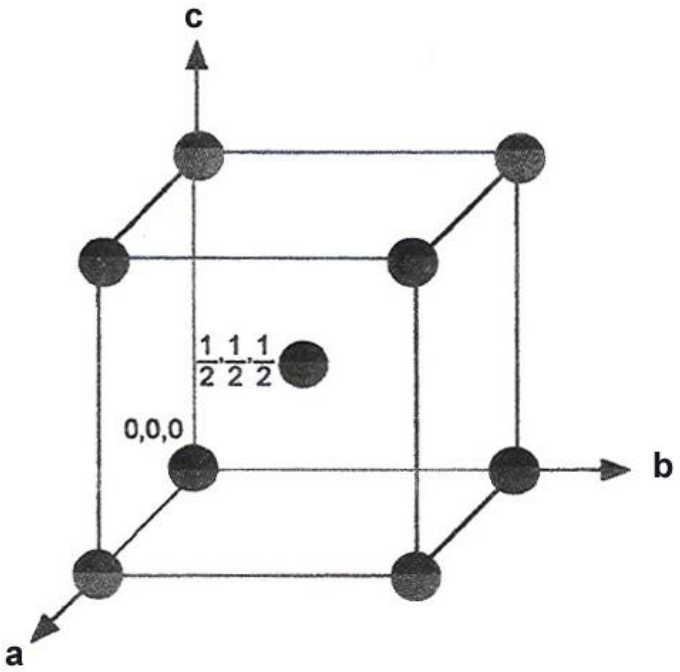
Crystallography

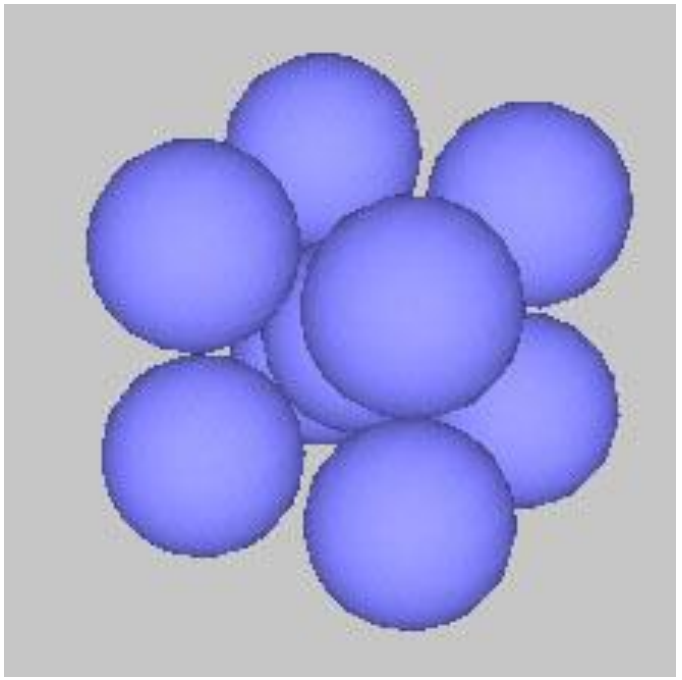
C. Crystal Structures

1. One atom per lattice point (basis)

b. Body-centered cubic (bcc)

Body-centered cubic (I) lattice + one atom ---> body-centered cubic (bcc) structure.





Body-centered cubic (bcc) structure.

Crystallography

C. Crystal Structures

1. One atom per lattice point (basis)

b. Body-centered cubic (bcc)

N = 2, we need two coordinates to define the cell. Start at 0,0,0, if translate a full lattice parameter will miss one atom, so must define atom in center as 1/2, 1/2, 1/2. (i.e. a translation of 1/2 a lattice parameter along each axis)

Examples: Na, W, Mo...

Crystallography

C. Crystal Structures

1. One atom per lattice point (basis)

c. Face-centered cubic (fcc)

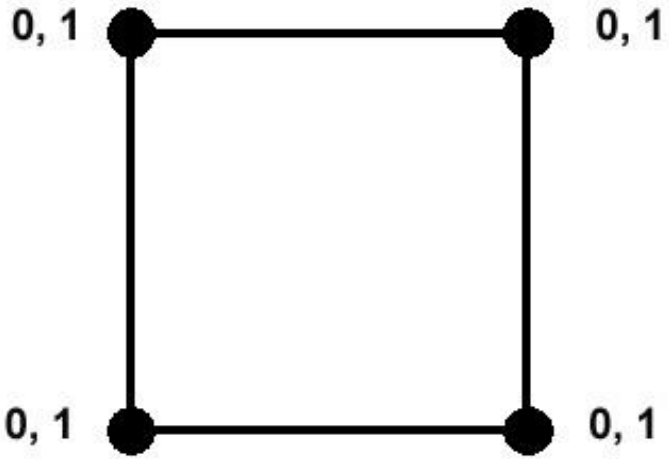
Homework: Define the fcc cell. What is N? Draw the crystal and planar representation.

Crystallography

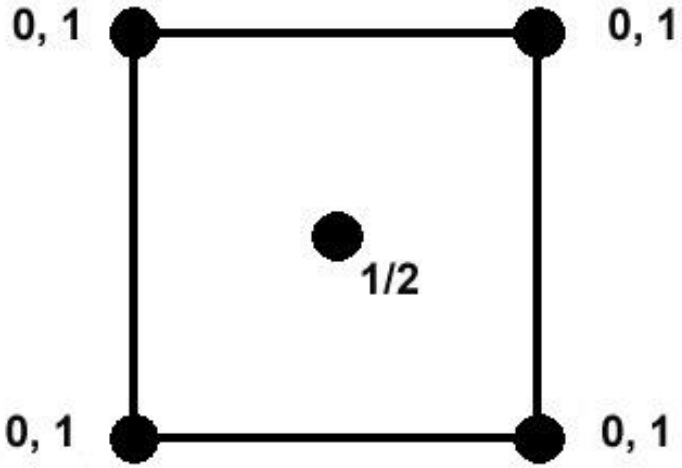
C. Crystal Structures

1. One atom per lattice point (basis)

Another type of notation to represent the cell is called a planar representation.



Simple cubic



Body-centered cubic

Crystallography

C. Crystal Structures

2. Two Atoms of the Same Kind per Lattice Point

a. Hexagonal Close Packed (hcp)

Hexagonal (P) lattice + 2 atoms ---> hcp structure

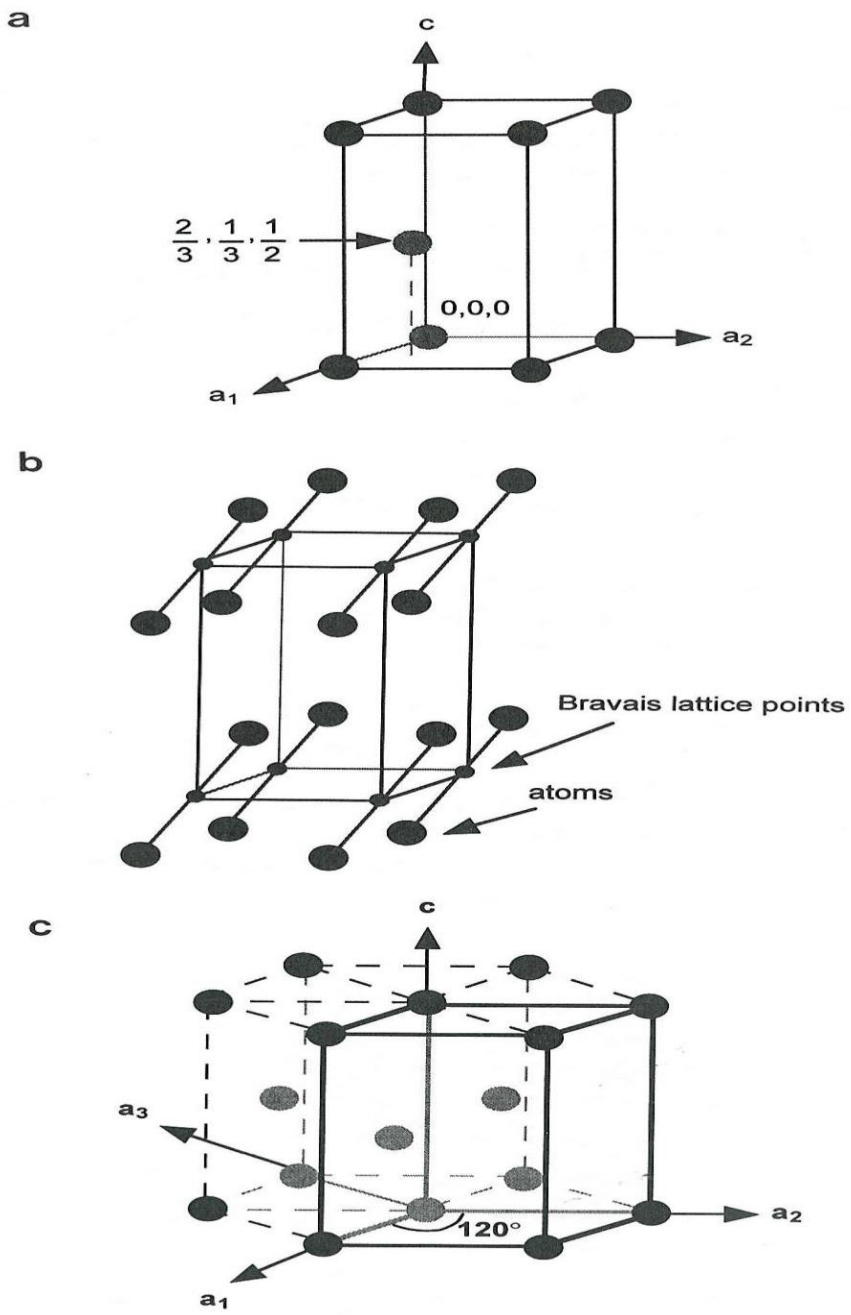


FIG. 22. Hexagonal close-packed structure.

Crystallography

C. Crystal Structures

2. Two Atoms of the Same Kind per Lattice Point

a. Hexagonal Close Packed (hcp)

Two atoms per unit cell at 0,0,0 and 2/3,1/3,1/2.

Since hcp is primitive, only one lattice point per cell, a pair of atoms is associated with each Bravais lattice point.

Crystallography

C. Crystal Structures

2. Two Atoms of the Same Kind per Lattice Point

b. Diamond Cubic Structure

Homework: Define the cell. What is N? Draw the crystal and planar representation.

Assignment

Read Chapter 2 from textbooks:

-X-ray Difffraction, A Practical Approach by Norton

-Introduction to X-ray powder
Diffractometry by Jenkins and Synder

-Elements of X-ray Diffraction by
Cullity and Stock

Homework 2: Due next tuesday

Define the fcc cell. What is N? Draw the crystal and planar representation.

Define the diamond cubic structure cell. What is N? Draw the crystal and planar representation.

Do UNT Bridge Module:
"Radiation Safety Training"