



CHEMISTRY 5570

Advanced Analytical Chemistry

X-ray Diffraction

Lecture 2

Dr. Teresa D. Golden

University of North Texas

Department of Chemistry

Advance X-Ray Diffraction

Class Website:

https://sites.chemistry.unt.edu/~tgolden/courses/course_downloadsFall24.xhtml

Readings:

Given at the end of each powerpoint lecture. The books are on reserve at the Willis library under CHEM 5390 (X-ray Diffraction).

Homework Assignments:

Given at the end of each powerpoint lecture. I do not accept assignments by email – all assignments must be turned in during class.

Exams:

There will be an exam in class on Tuesday, December 10th, 8:00 - 10:00 a.m.



Important for Calculations

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

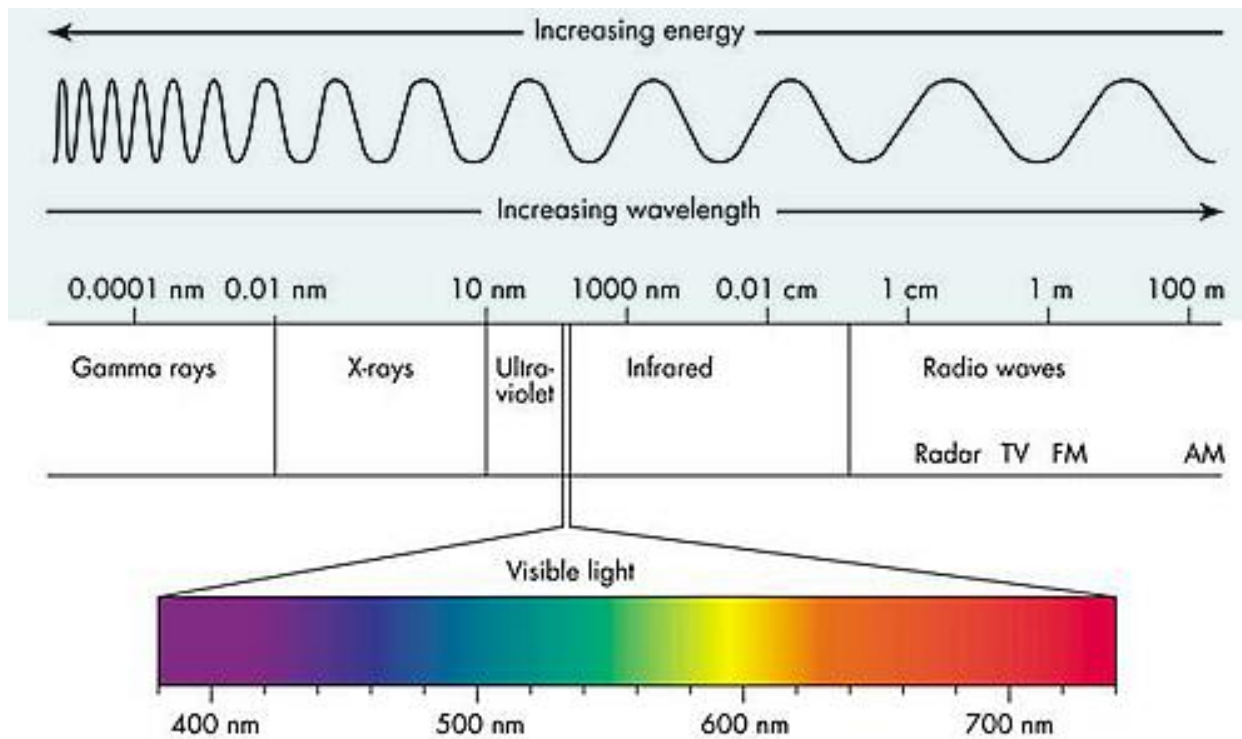
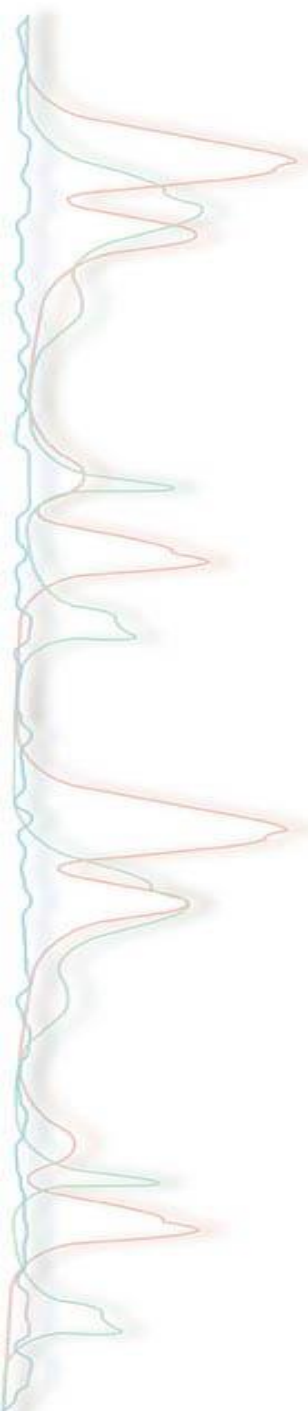
where n is an integer

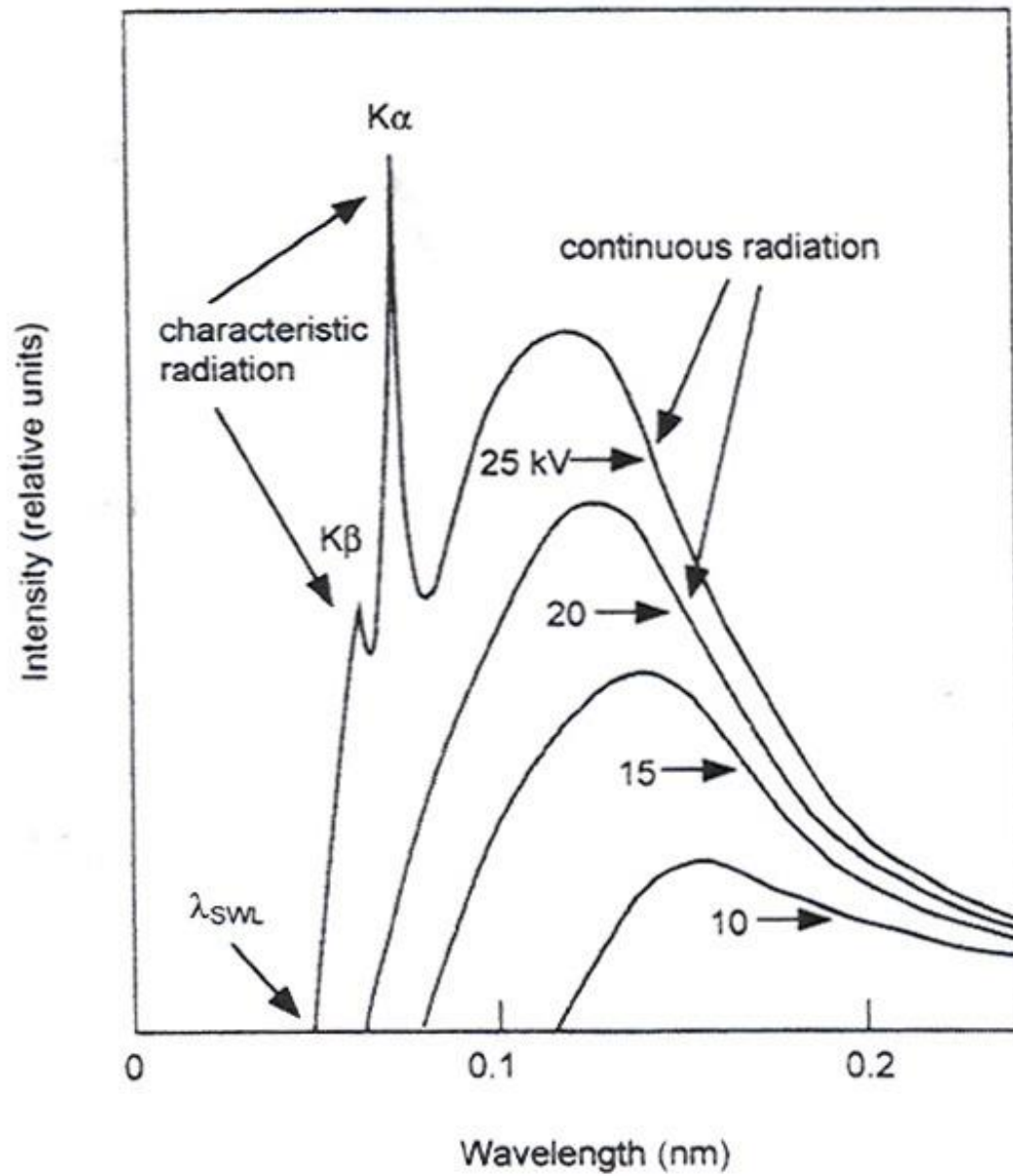
λ is the wavelength of the x-rays

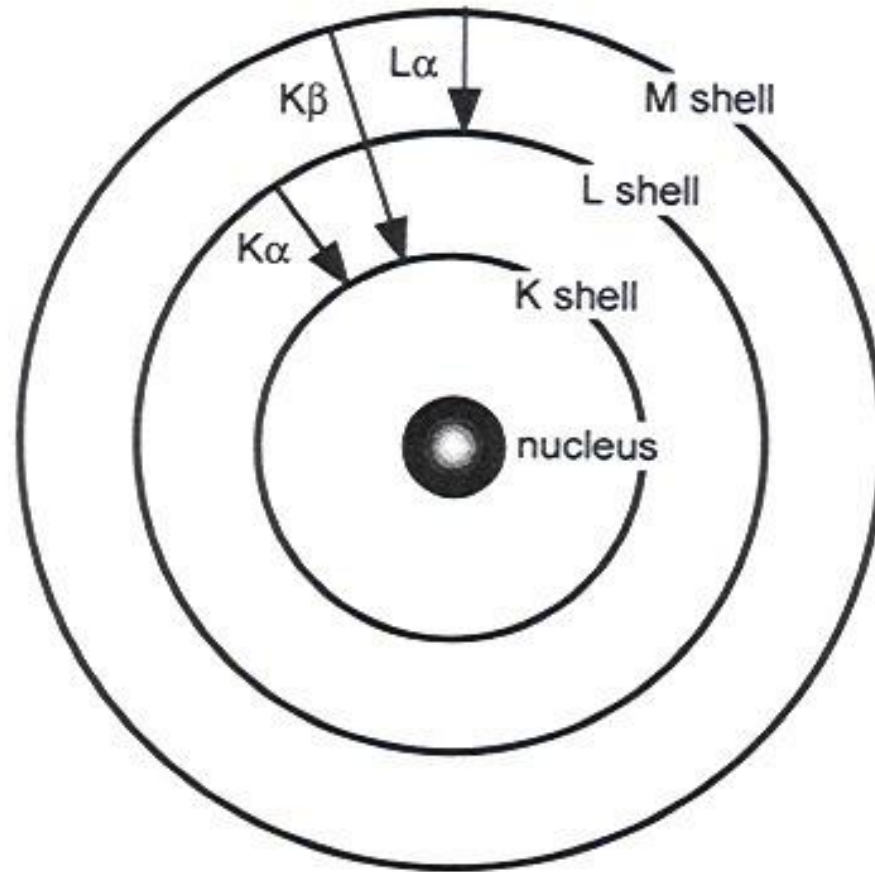
d is the interplanar spacing in the specimen

θ is the diffraction angle

Bragg Equation



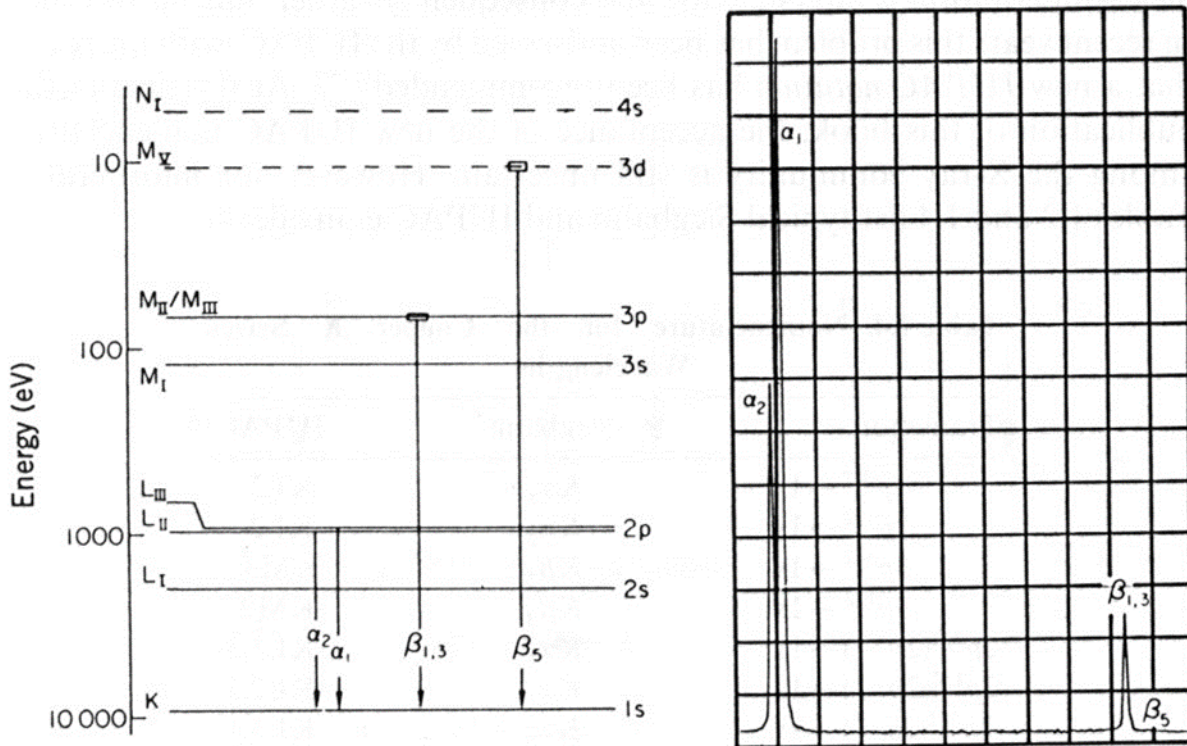




Electron transitions in an atom, which produce the $K\alpha$, $K\beta$ and $L\alpha$ characteristic x-rays.

Properties of X-rays

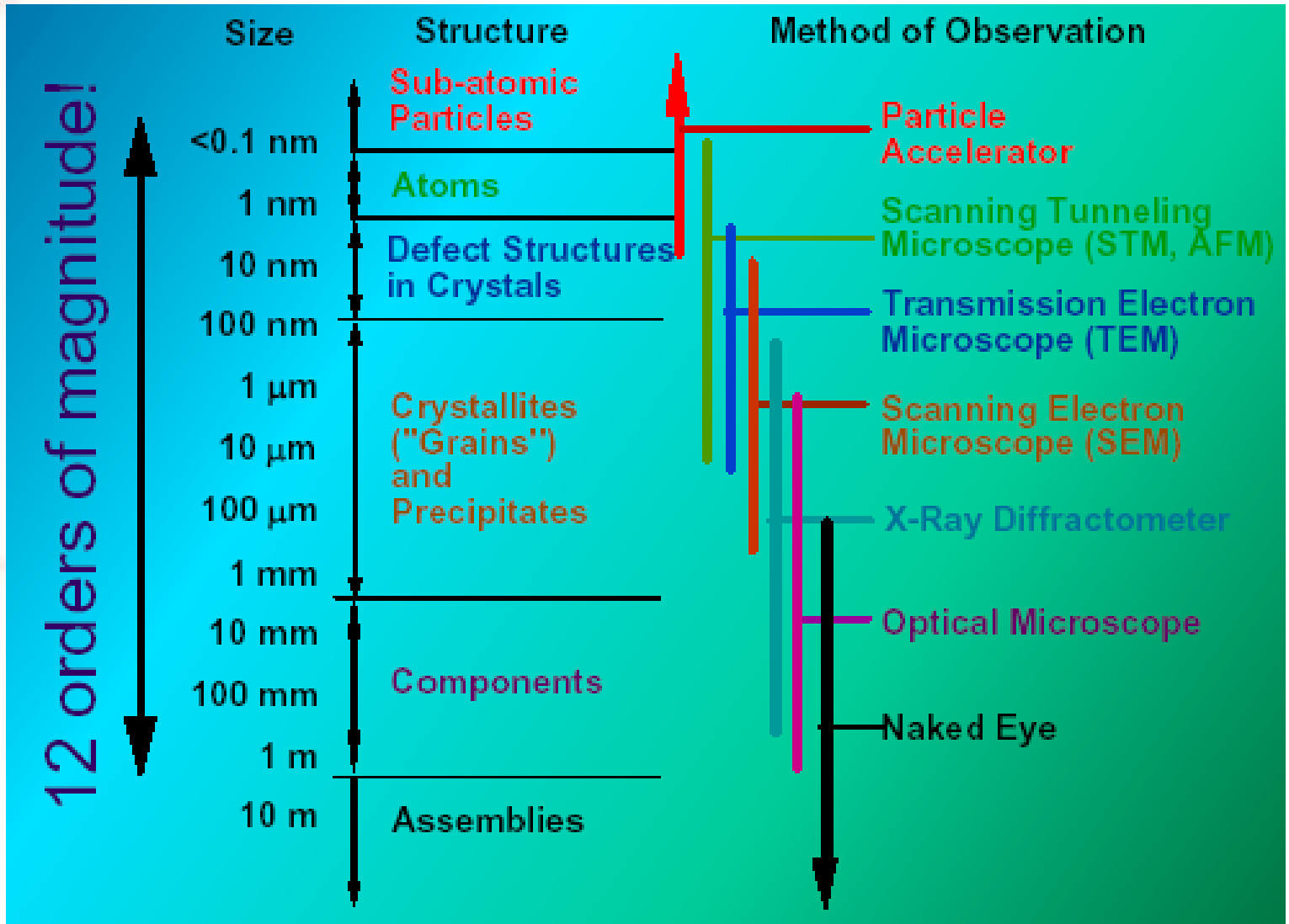
The Copper K Spectrum



The copper $K\alpha$ spectrum.

- The diagram at left shows the 5 possible Cu K transitions
- L to K “jumps”:
 - $K\alpha_1$ (8.045 keV, 1.5406Å)
 - $K\alpha_2$ (8.025 keV, 1.5444Å)
- M to K
 - $K\beta_1$ $K\beta_3$ (8.903 keV, 1.3922Å)
 - $K\beta_5$

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 $\sim 2-3$ Å so the suitable radiation is X-rays

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

Crystallography

Monochromatic X-rays

Many θ s (orientations)
Powder specimen

POWDER
METHOD

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

Panchromatic X-rays

Single θ

LAUE
TECHNIQUE

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

Monochromatic X-rays

θ Varied by rotation

ROTATING
CRYSTAL
METHOD

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

Crystallography

Geometry and the structure of crystals

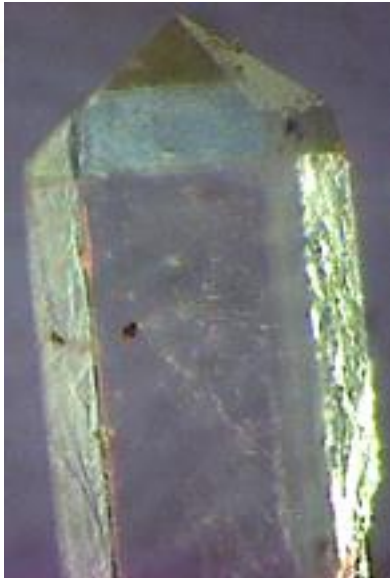
Lattices

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

Crystallography

Geometry and the structure of crystals

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



Crystallography

Geometry and the structure of crystals

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

Amorphous – 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 can range from amorphous to semi-crystalline

The crystal structure directly influences the properties of the material

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

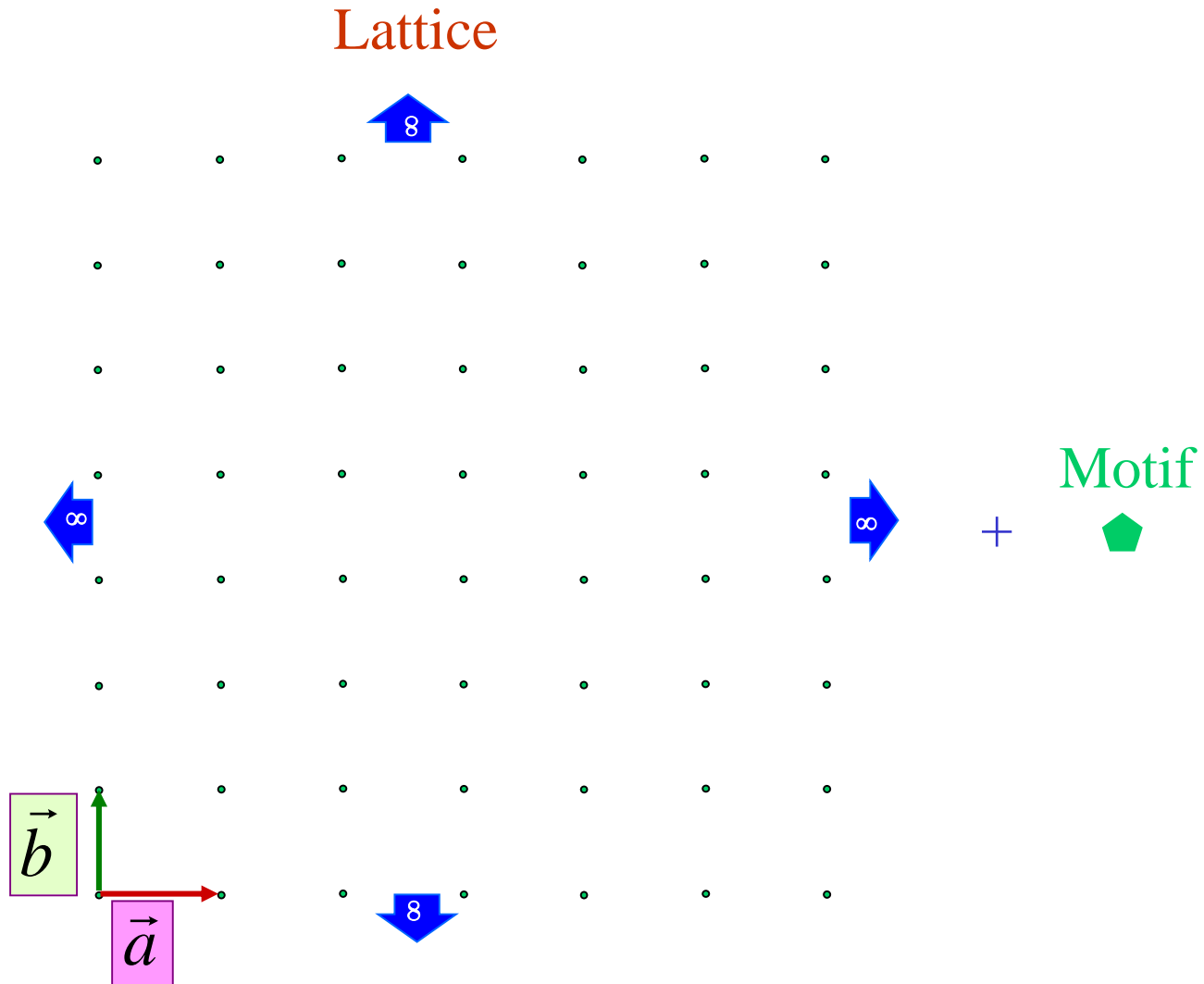
Translationally periodic
arrangement of points

Crystal

Translationally periodic
arrangement of motifs (basis)

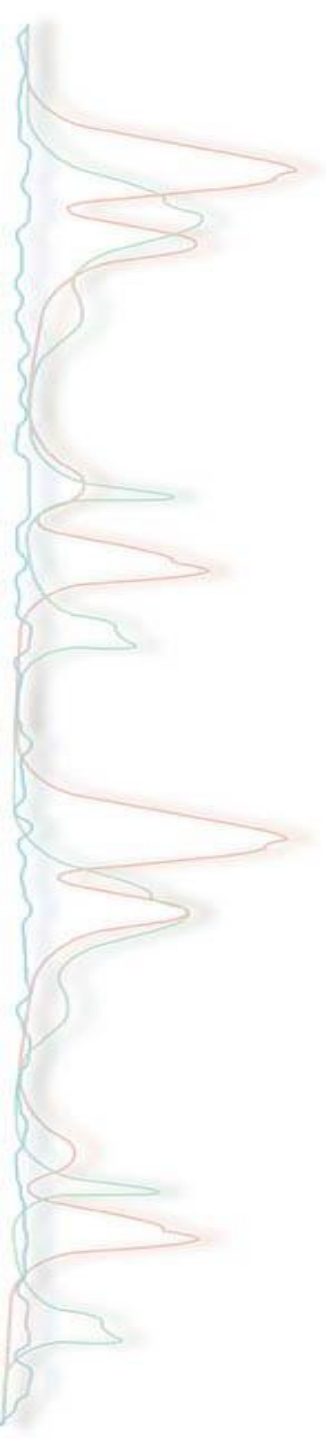
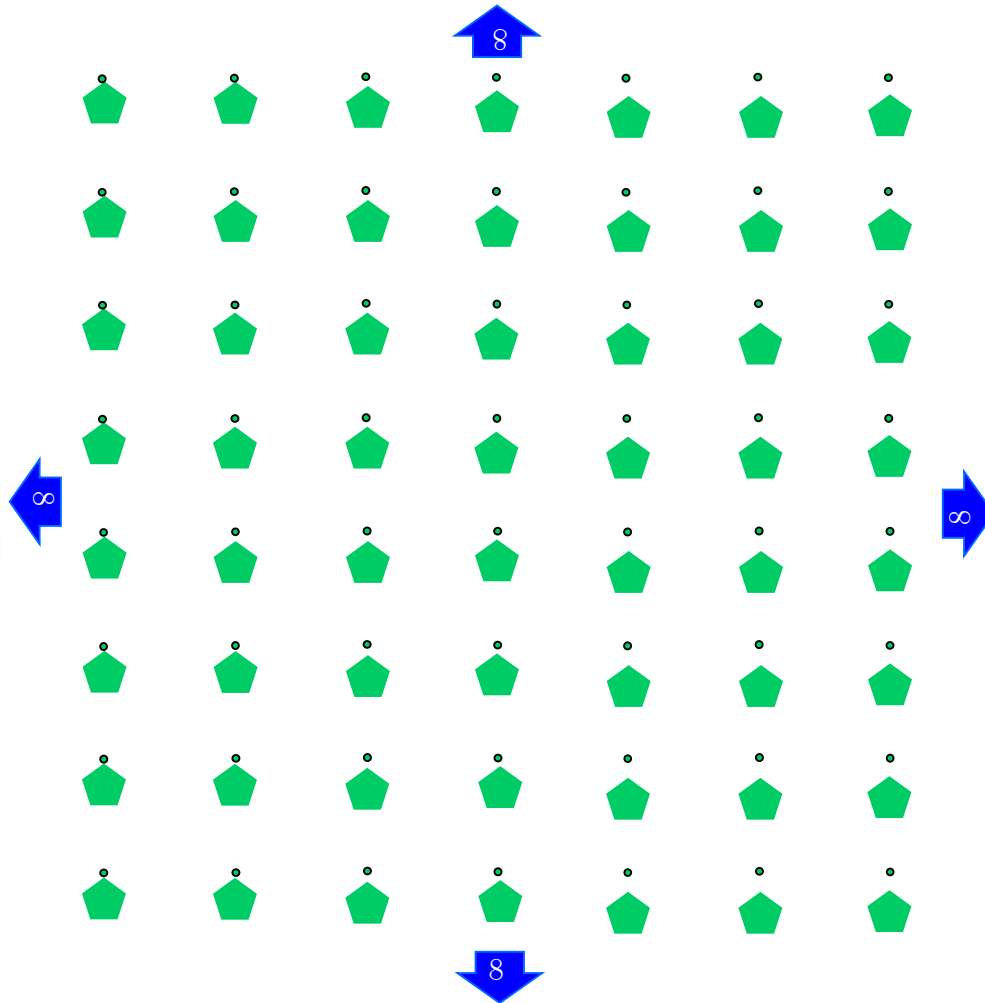
Crystallography

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

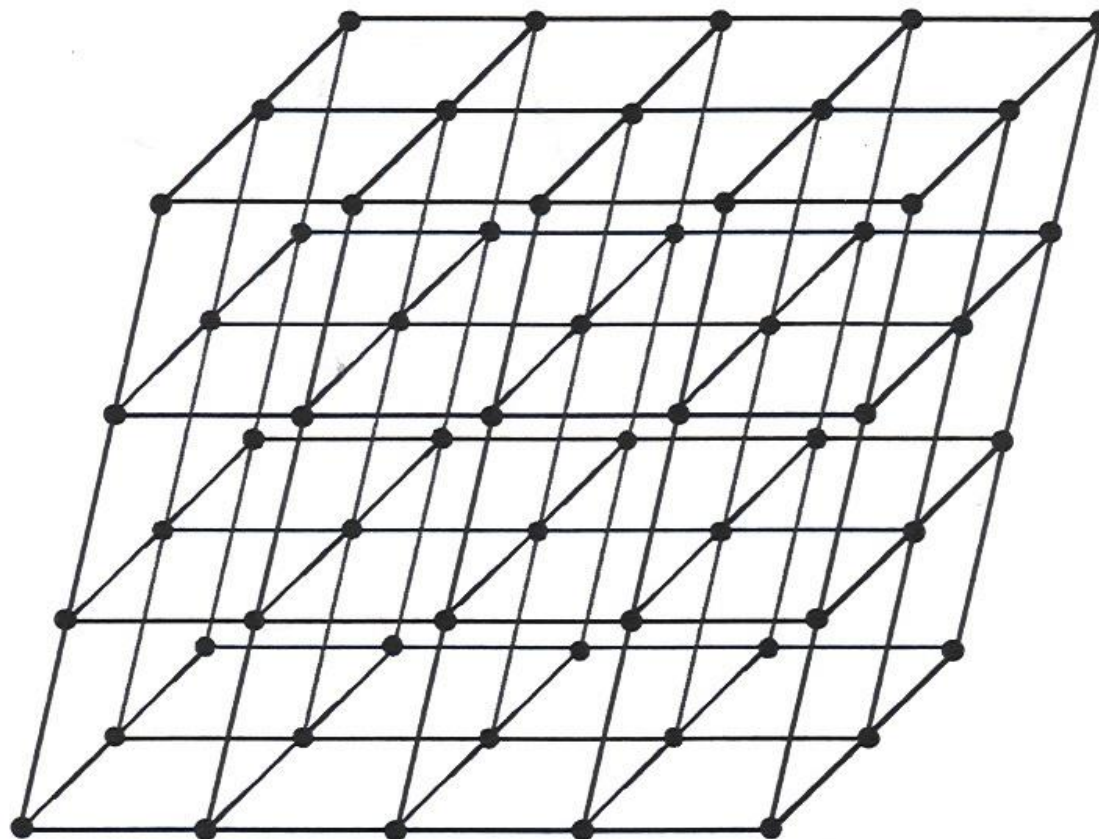
Geometry and the structure of crystals

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

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

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

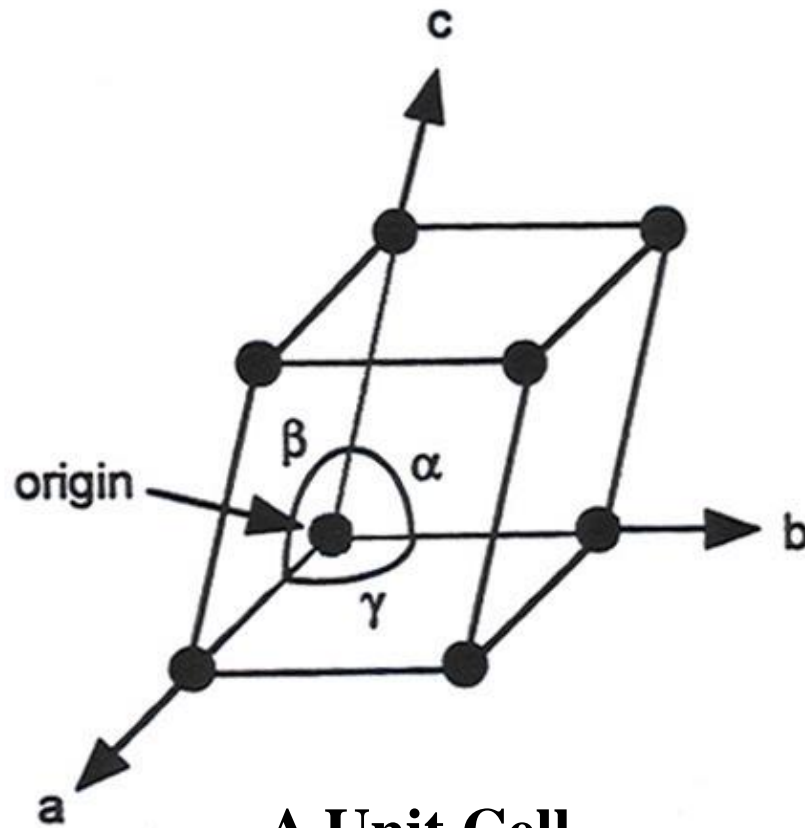
Lattices

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

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.

$$a = b = c$$

$$\alpha = \beta = \gamma = 90^\circ$$

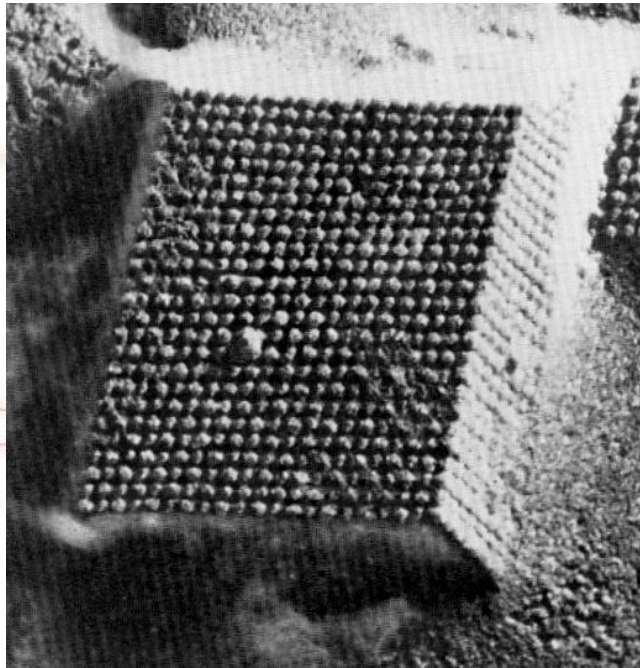
Crystallography

B. Crystal Systems

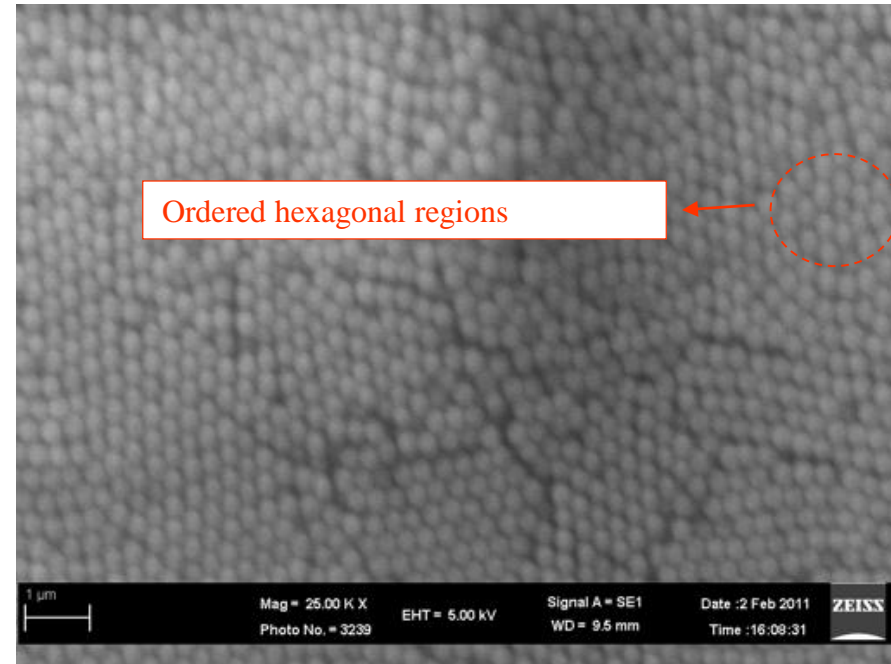
- Crystals can have a wide range of lattice parameter sizes ranging from
 - Small unit cells (a_{Cu} (FCC)= 3.61 Å)
 - to
 - Medium sized UC ($a_{\text{Fullerene}}$ (FCC)= 14.17 Å)
 - to
 - Large unit cells ($a_{\text{CPV virus}^*}$ (BCC) = 103.7 Å)
- Typically colloidal and organic crystals have large unit cells
- An example of colloidal crystal is silica nanospheres forming a 2D crystal with 4-fold symmetry.

Crystallography

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

Crystal Systems

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

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 (<i>two will generate the other two</i>)
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.

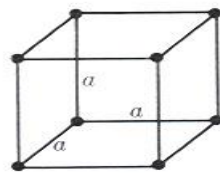
Crystal systems and Bravais lattices.

Crystallography

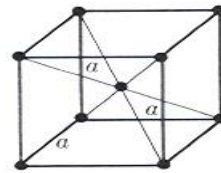
Geometry and the structure of crystals

Crystal Systems

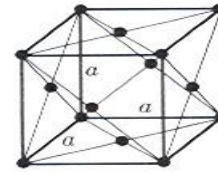
Within the crystal systems, there are 14 possible point lattices called Bravais lattices or point lattices (discovered by Bravais in 1848).



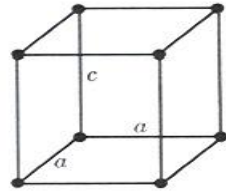
SIMPLE CUBIC (P)



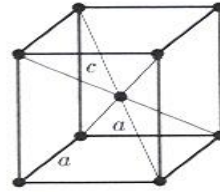
BODY-CENTERED CUBIC (I)



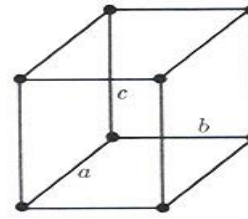
FACE-CENTERED CUBIC (F)



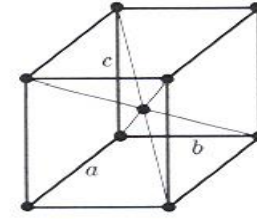
SIMPLE TETRAGONAL (P)



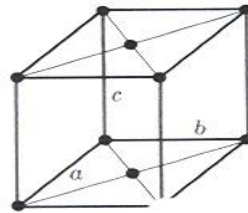
BODY-CENTERED TETRAGONAL (I)



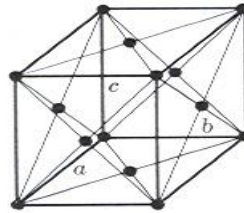
SIMPLE ORTHORHOMBIC (P)



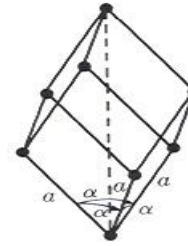
BODY-CENTERED ORTHORHOMBIC (I)



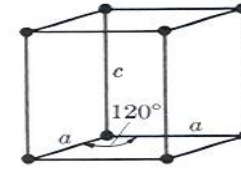
BASE-CENTERED ORTHORHOMBIC (C)



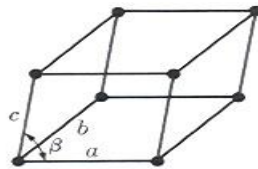
FACE-CENTERED ORTHORHOMBIC (F)



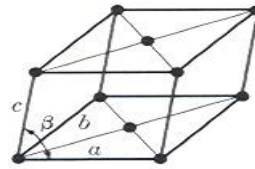
RHOMBOHEDRAL (R)



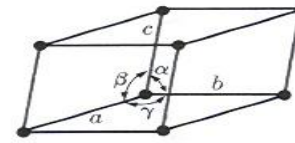
HEXAGONAL (P)



SIMPLE MONOCLINIC (P)



BASE-CENTERED MONOCLINIC (C)



TRICLINIC (P)

The fourteen Bravais lattices.

Crystallography

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

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

Crystal Systems

Number of lattice points per cell is:

$$N = N_i + N_f/2 + N_c/8$$

N_i - number of interior points.

N_f - number of points on faces (shared).

N_c - number of points on corners (shared).

Crystallography

Crystal Systems

Example:

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

$$N = N_i + N_f/2 + N_c/8 = 0 + 0 + 8/8 = 1$$

For cubic I, what is N?

$$N = 1 + 0 + 8/8 = 2$$

For cubic F, what is N?

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

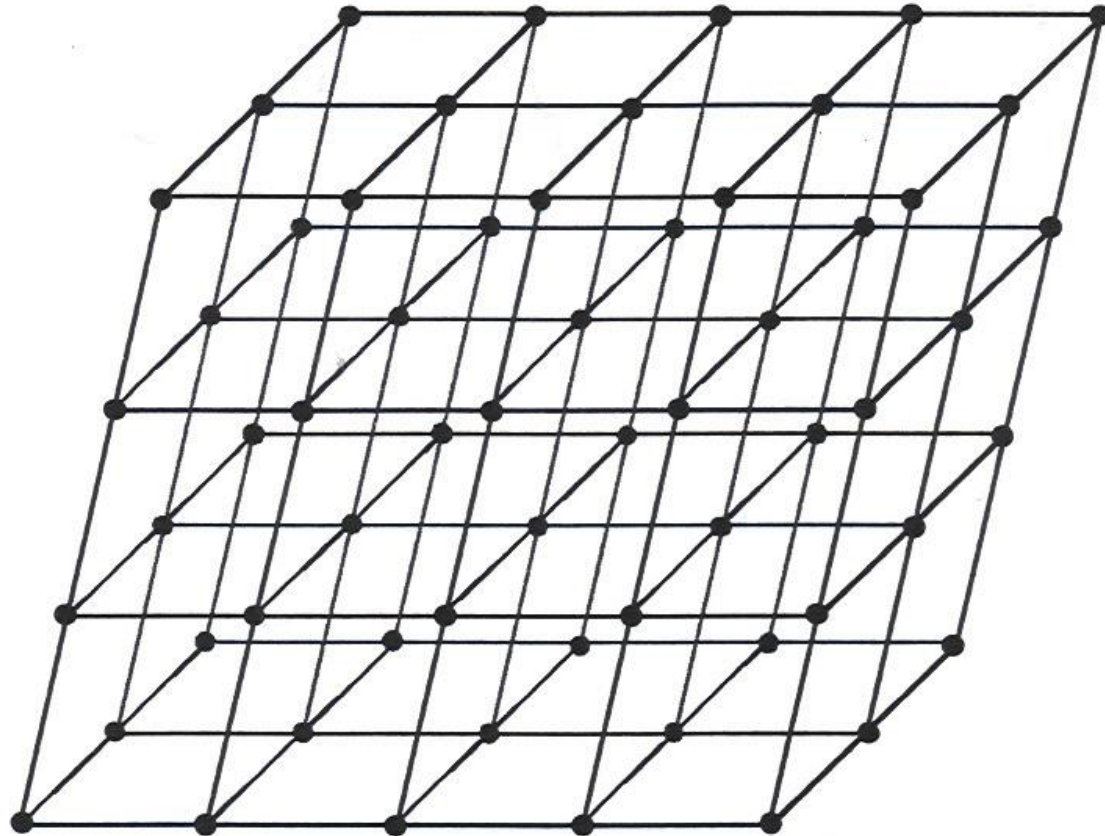


Crystallography

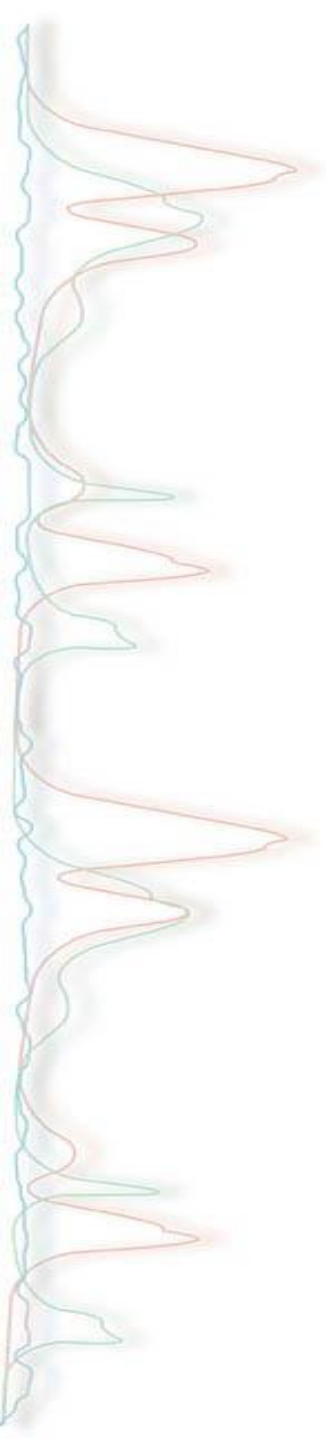
Crystal Systems

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

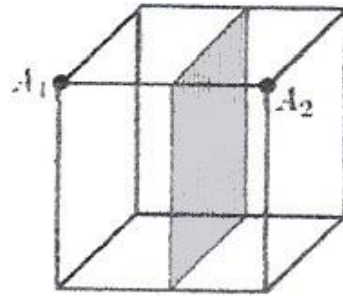
Crystal Systems

Symmetry

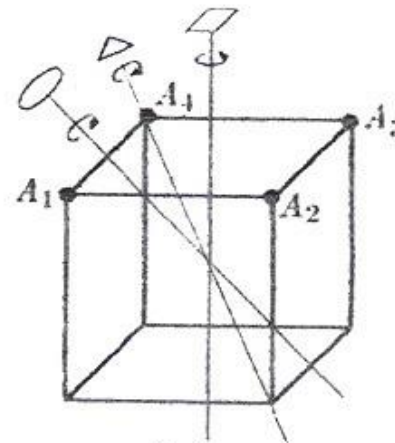
Both Bravais lattices and real crystals exhibit various kinds of symmetry. This symmetry is represented by symmetry operations.

These include:

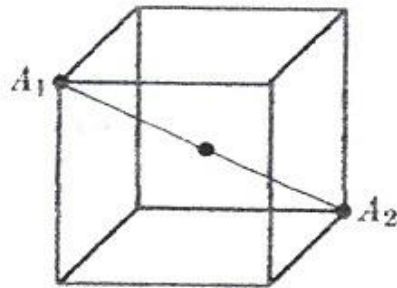
- reflection
- rotation
- inversion
- rotation-inversion



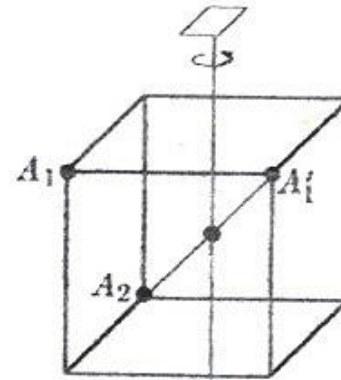
(a)



(b)



(c)



(d)

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

Crystal Systems

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 possess a certain minimum set of symmetry elements.

Crystallography

Crystal Systems

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.

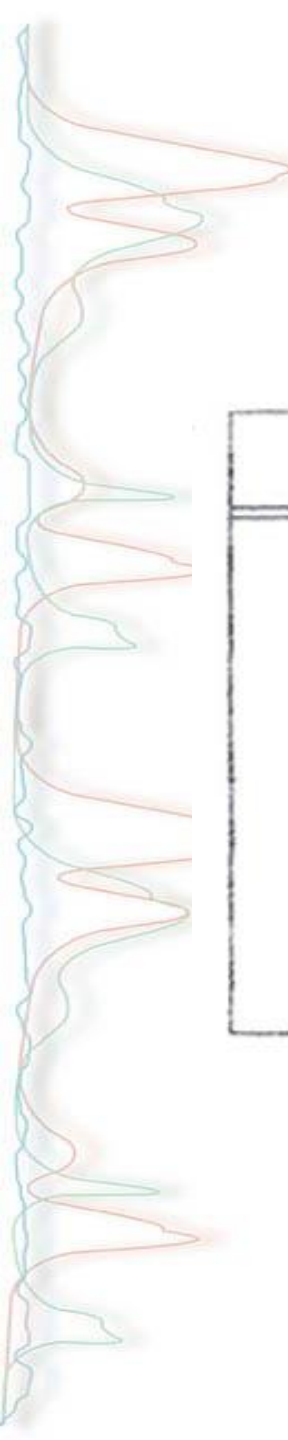
Crystallography

Crystal Systems

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

Crystal Systems

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.

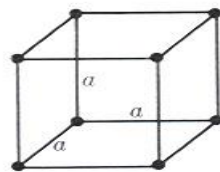
Crystallography

Crystal Structures

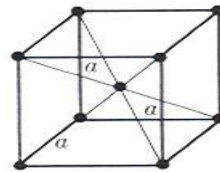
Relate Bravais lattices with actual crystal structure using a basis.

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

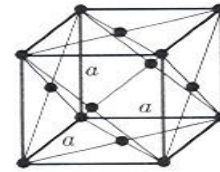
Bravais lattice + basis \rightarrow Crystal system



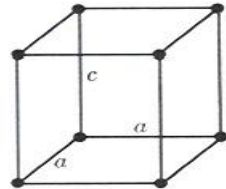
SIMPLE CUBIC (P)



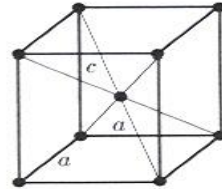
BODY-CENTERED CUBIC (I)



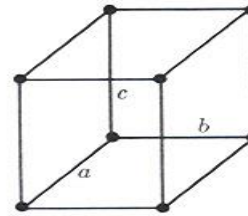
FACE-CENTERED CUBIC (F)



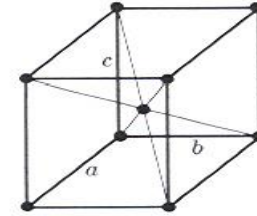
SIMPLE TETRAGONAL (P)



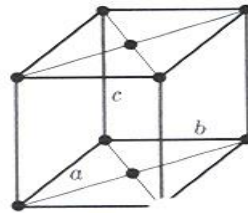
BODY-CENTERED TETRAGONAL (I)



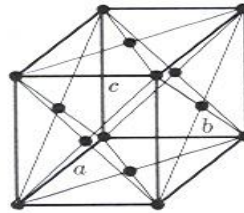
SIMPLE ORTHORHOMBIC (P)



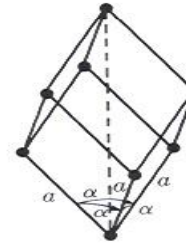
BODY-CENTERED ORTHORHOMBIC (I)



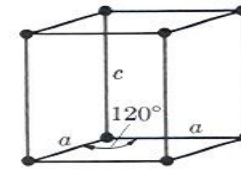
BASE-CENTERED ORTHORHOMBIC (C)



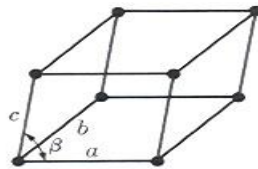
FACE-CENTERED ORTHORHOMBIC (F)



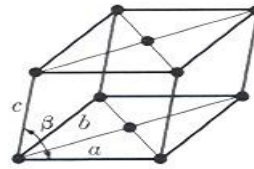
RHOMBOHEDRAL (R)



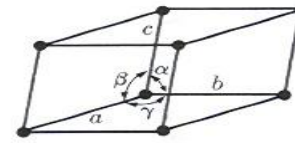
HEXAGONAL (P)



SIMPLE MONOCLINIC (P)



BASE-CENTERED MONOCLINIC (C)



TRICLINIC (P)

The fourteen Bravais lattices.

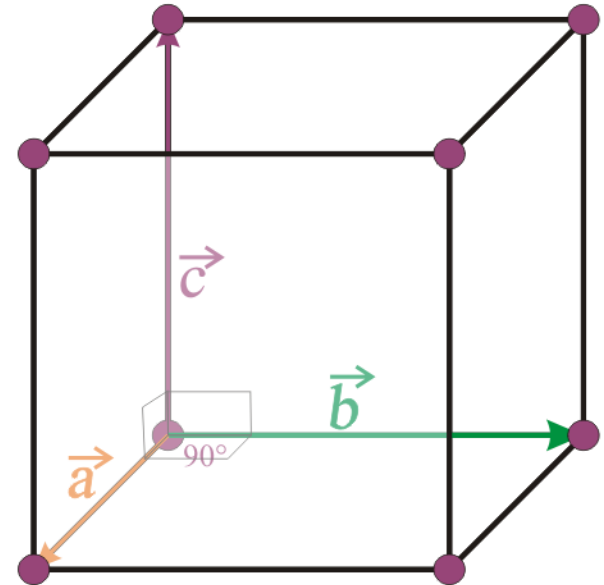
Crystallography

Cubic Crystals

$$a = b = c$$

$$\alpha = \beta = \gamma = 90^\circ$$

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



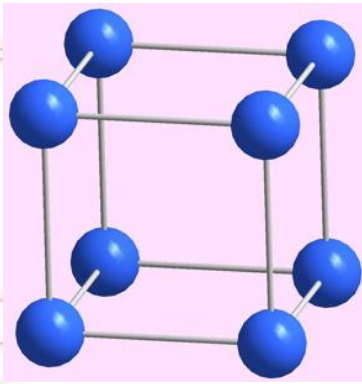
- | | |
|-----------------------------------|---------------------------------|
| ▪ Elements with Cubic structure → | SC: F, O, Po |
| | BCC: Cr, Fe, Nb, K, W, V |
| | FCC: Al, Ar, Pb, Ni, Pd, Pt, Ge |

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

Crystallography

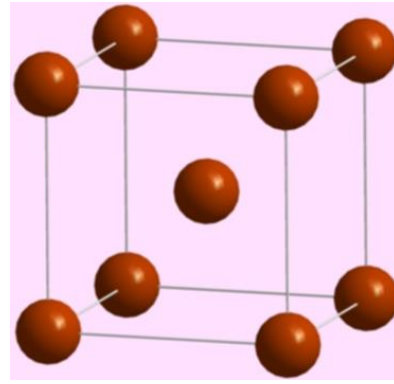
B. Crystal Systems

Examples of Cubic Crystal Structure



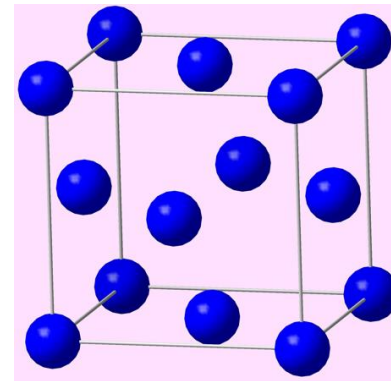
$n = 1$

SC



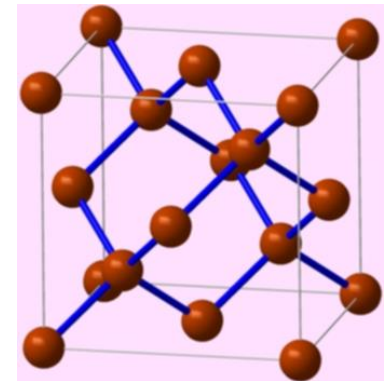
$n = 2$

BCC



$n = 4$

FCC/CCP



$n = 8$

DC

C (diamond)

Crystallography

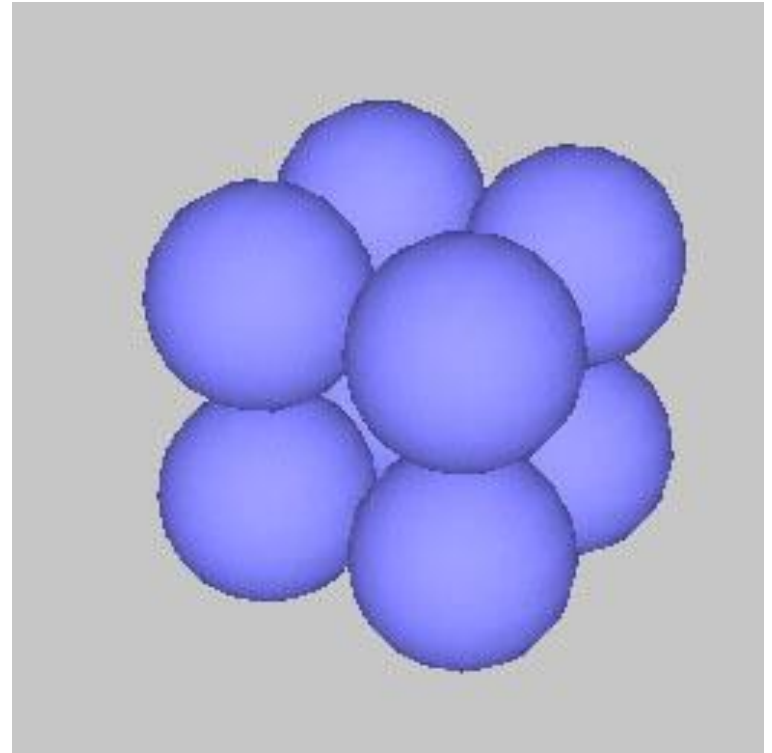
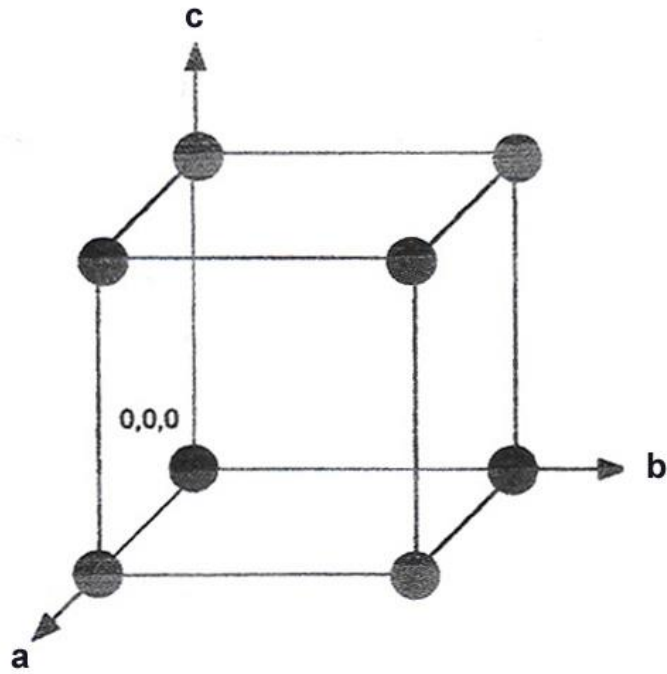
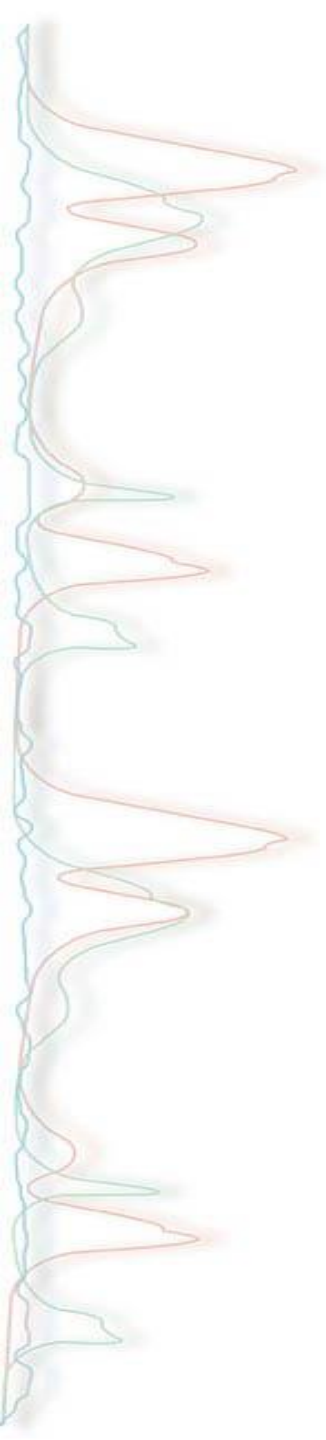
Crystal Structures

One atom per lattice point (basis)

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

Primitive cubic

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



Simple cubic structure.

Crystallography

Crystal Structures

One atom per lattice point (basis)

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

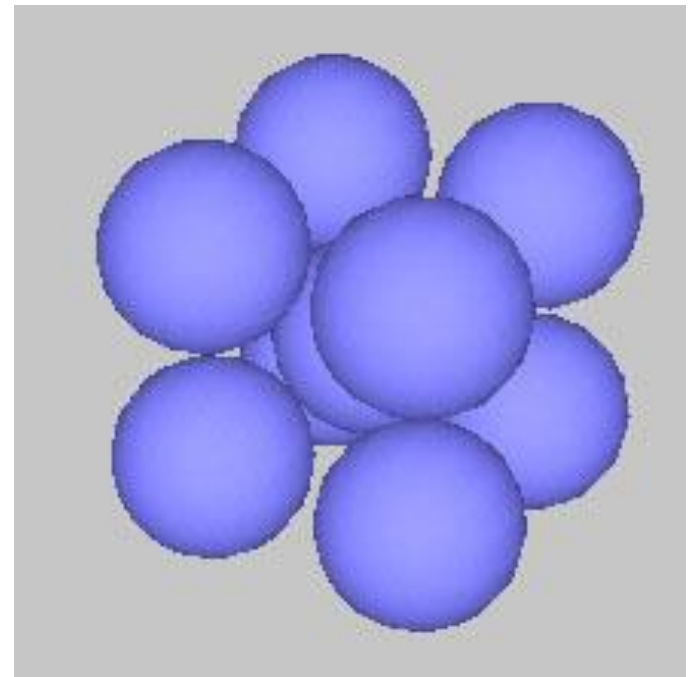
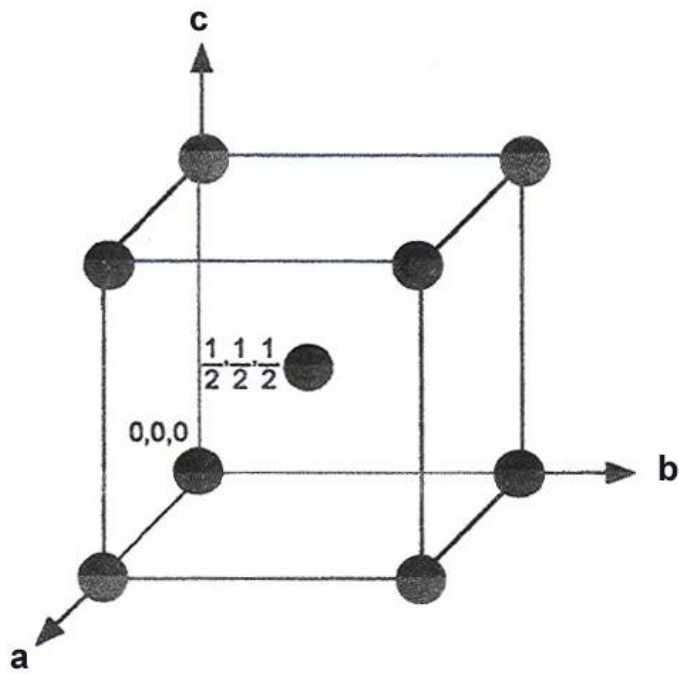
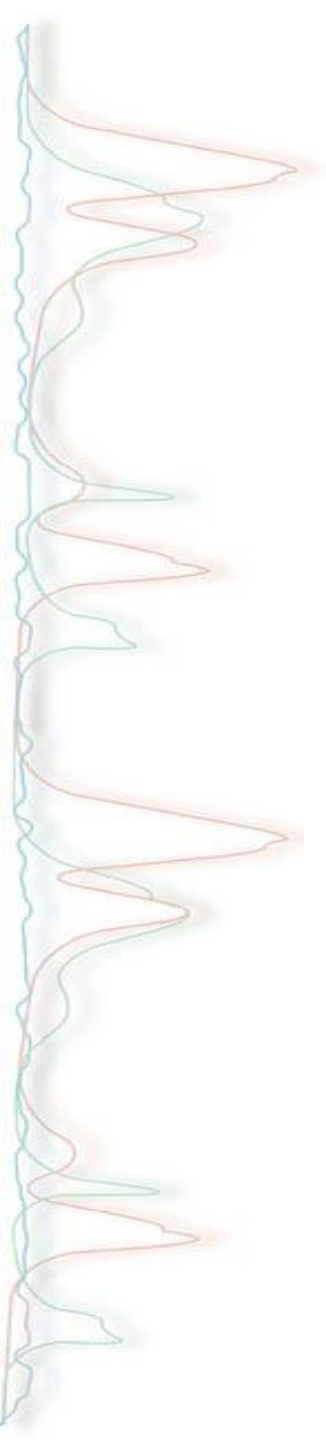
Crystallography

Crystal Structures

One atom per lattice point (basis)

Body-centered cubic (bcc)

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



Body-centered cubic (bcc) structure.

Crystallography

Crystal Structures

One atom per lattice point (basis)

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

Crystal Structures

One atom per lattice point (basis)

Face-centered cubic (fcc)

(Homework 2: See end of lecture assignment slide)

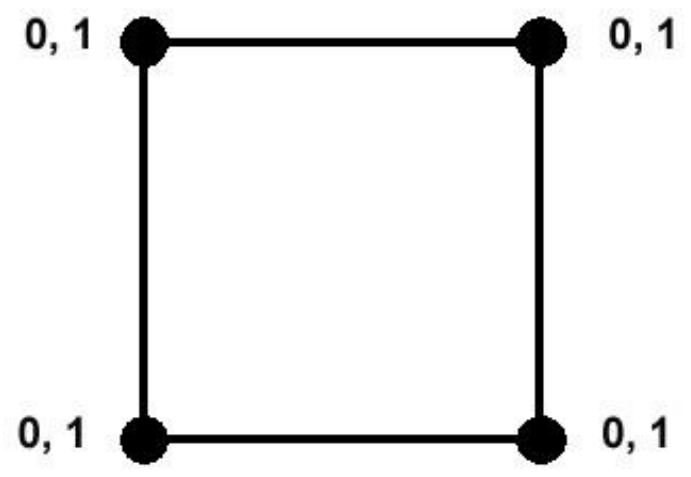
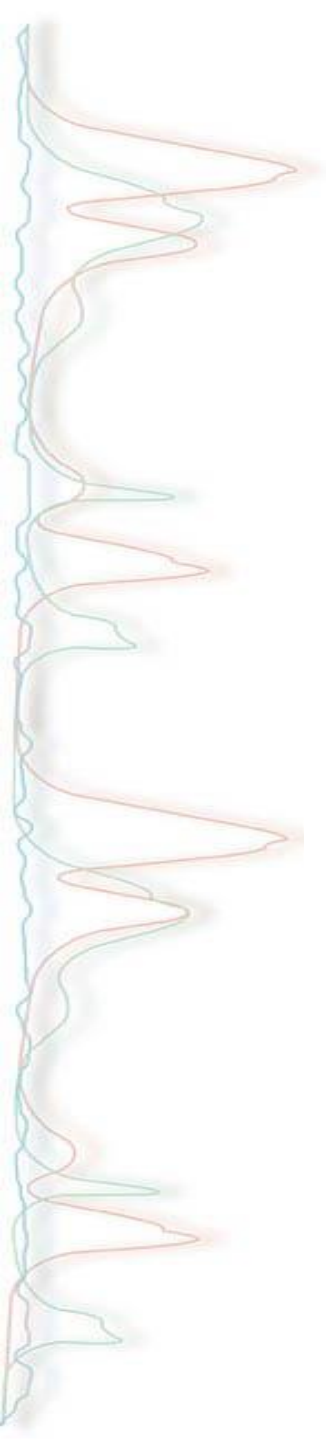


Crystallography

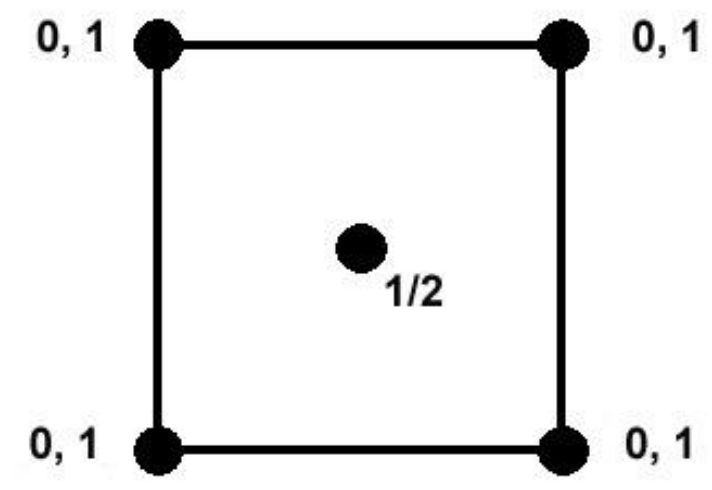
Crystal Structures

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

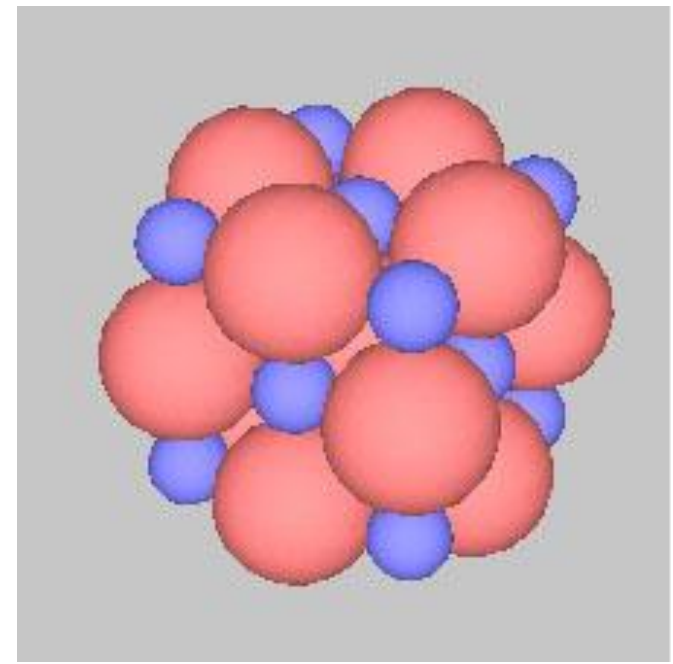
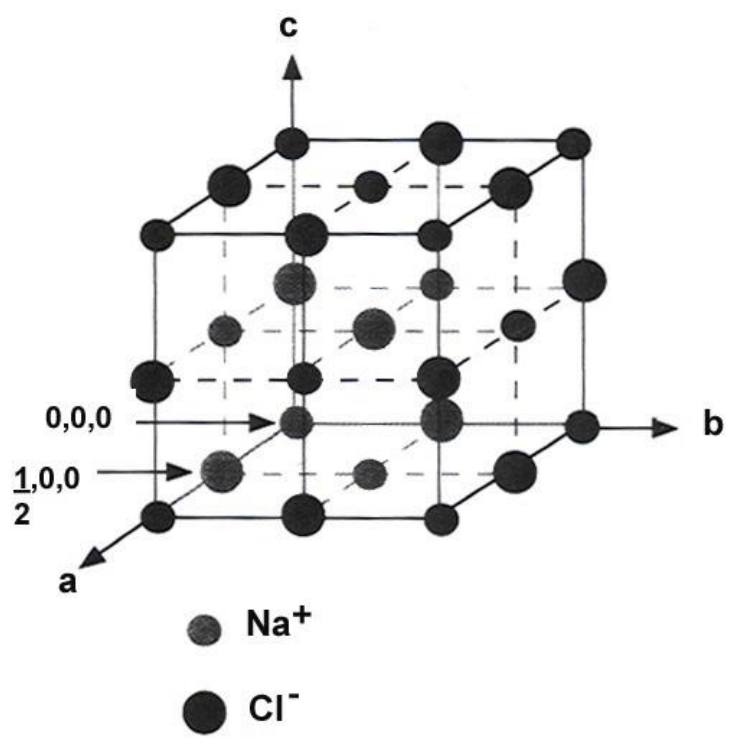
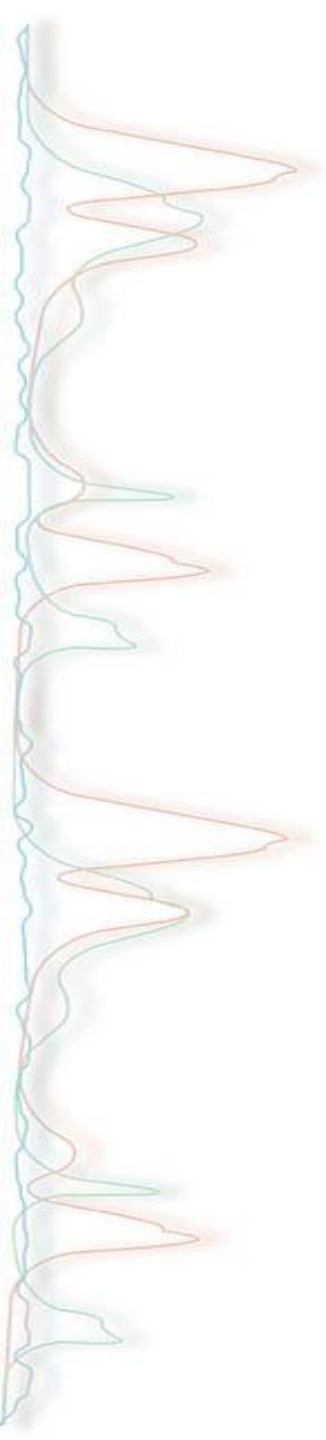
Crystal Structures

Two Different Atoms per Lattice Point

Sodium Chloride Structure or Rocksalt Structure

Face-centered cubic (F) lattice + 2 atoms --->
Rocksalt structure

There are a basis of two atoms at $0, 0, 0$, for Na and $1/2, 0, 0$ for Cl.



Sodium Chloride (NaCl) structure.

Crystallography

Crystal Structures

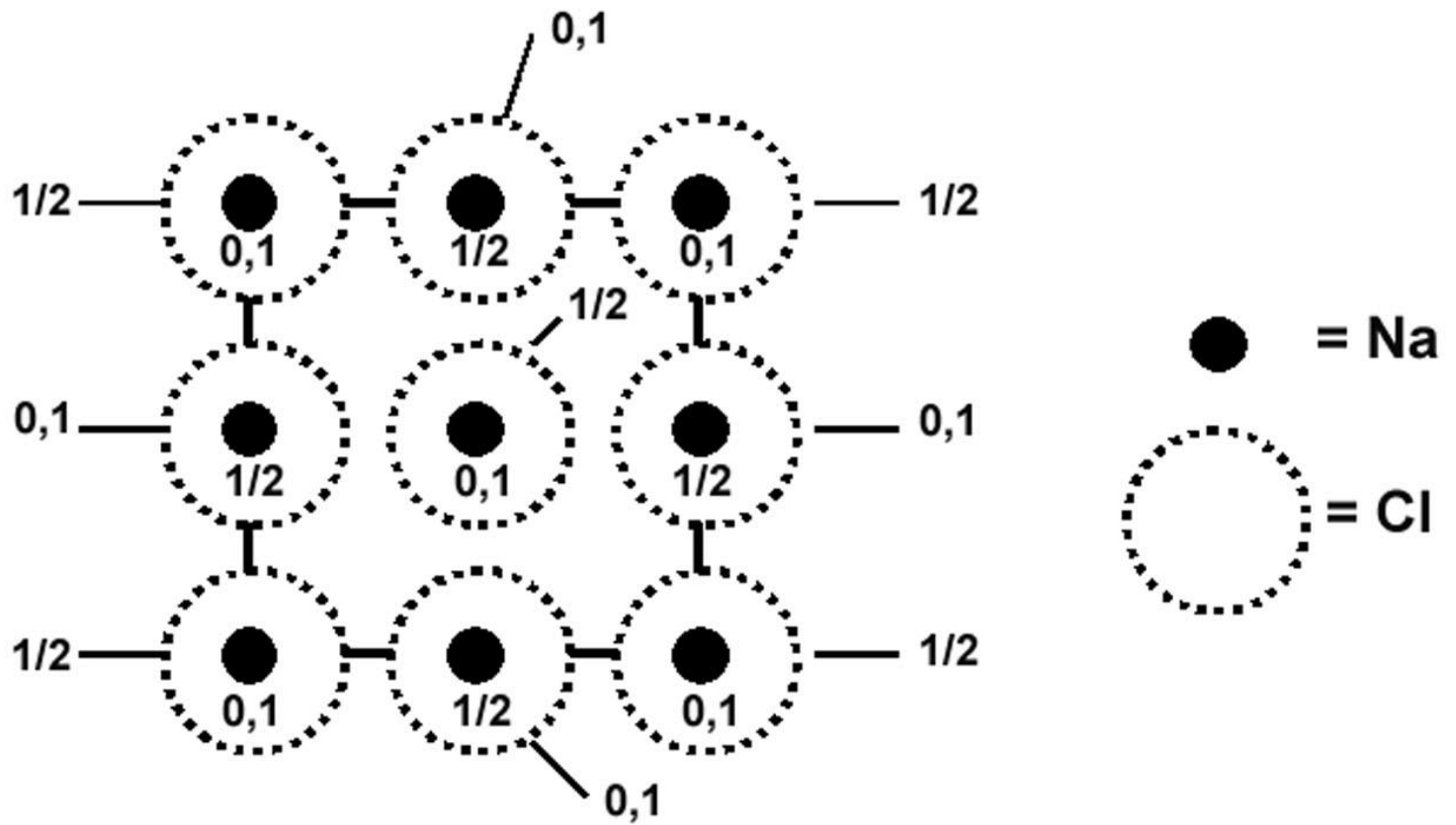
Two Different Atoms per Lattice Point

Sodium Chloride Structure or Rocksalt Structure

Na at 0, 0, 0	1/2, 1/2, 0	1/2, 0, 1/2	0, 1/2, 1/2
Cl at 1/2, 0, 0	0, 1/2, 0	0, 0, 1/2	1/2, 1/2, 1/2

Na atoms are in a face centered cubic arrangement, translate $1/2$ and Cl is also in face centered cubic arrangement.

What would the planar representation look like?



Planar representation of sodium chloride structure.

Crystallography

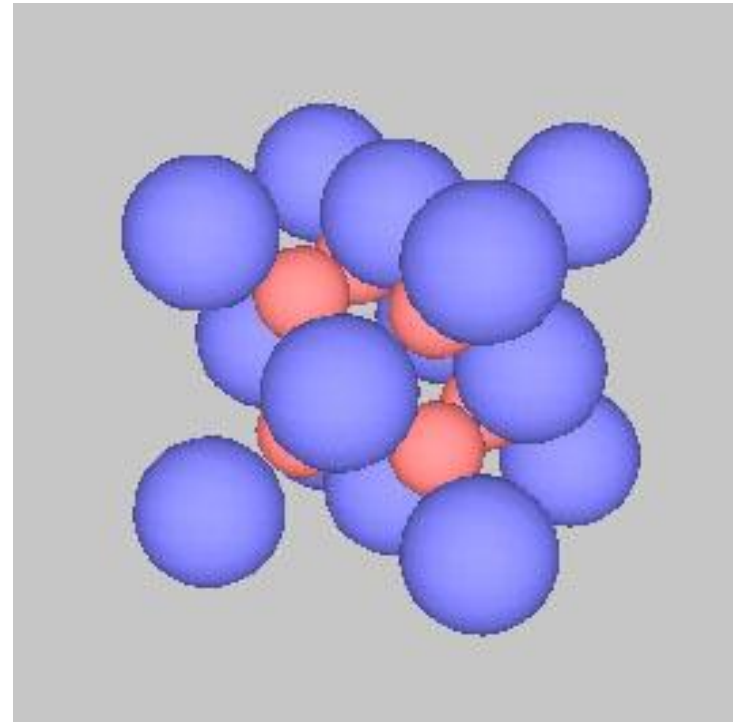
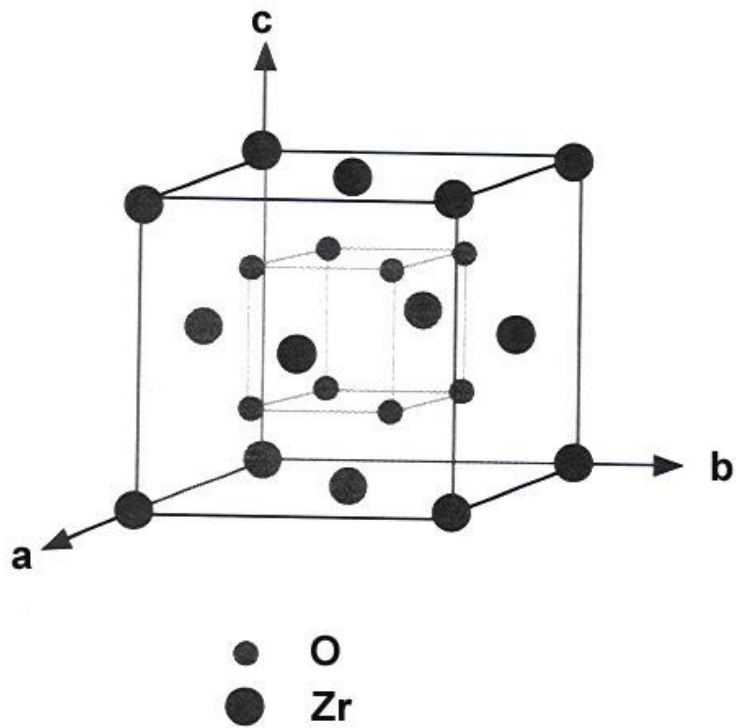
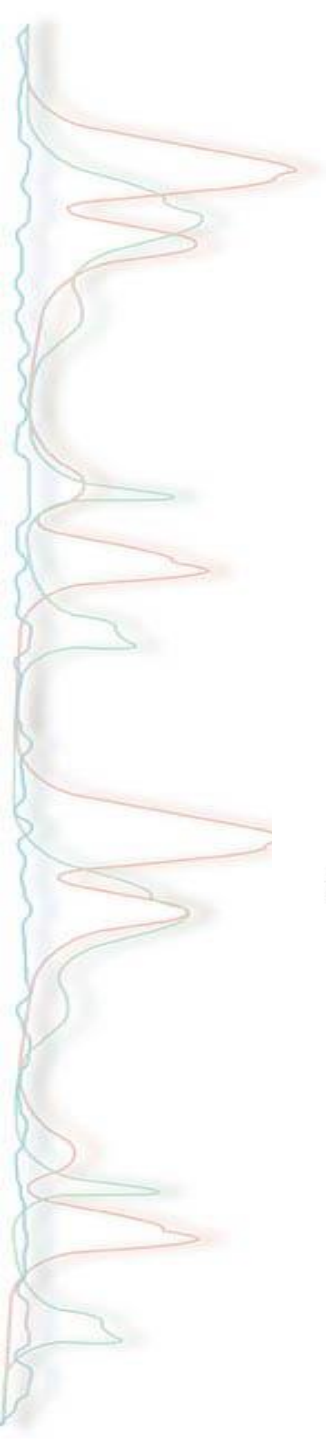
Crystal Structures

More complex structures

Can have more than two atoms associated with each lattice point.

Common example:

Face centered cubic lattice + 3 atoms ---> Fluorite structure



Fluorite Structure.

Crystallography

Crystal Structures

More complex structures

Name of Structure	Corresponding Materials	Other Materials
Rocksalt	NaCl	KCl, LiF, MgO, TiN
Zinc blende	ZnS	BeO, GaAs, β -SiC
Rutile	TiO ₂	GeO ₂ , SnO ₂
Corundum	Al ₂ O ₃	Fe ₂ O ₃ , Cr ₂ O ₃
Wurtzite	ZnS	ZnO, AlN, α -SiC
Perovskite	CaTiO ₃	BaTiO ₃ , SrTiO ₃
Spinel	MgAl ₂ O ₄	FeAl ₂ O ₄ , ZnAl ₂ O ₄

Crystallography

Crystal Structures

Online tools

<https://crystals.symotter.org/viztools/>

<https://www.jove.com/v/10462/single-crystal-and-powder-x-ray-diffraction>

<https://www.jove.com/v/10446/x-ray-diffraction-for-determining-atomic-and-molecular-structure>

https://myscope.training/XRD_XRD_basics

Assignments

UNT Bridge Module:

“Radiation Safety Training”

You must make a copy of your successful completion of this training and give to Dr. Golden - Due Today.

Homework Assignment 1 – Due Today.

Homework Assignment 2: Due Wednesday 11-20-24

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

Read this website page and listen to the videos:

<https://www.sciencemuseum.org.uk/objects-and-stories/chemistry/x-ray-crystallography-revealing-our-molecular-world>

Read Chapters 1&2 from the following textbooks:

- X-ray Diffraction, A Practical Approach by Norton**
- Elements of X-ray Diffraction by Cullity and Stock**
- Introduction to X-ray powder Diffractometry by Jenkins and Synder**

