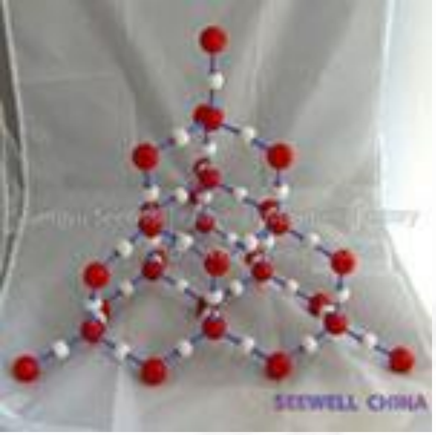
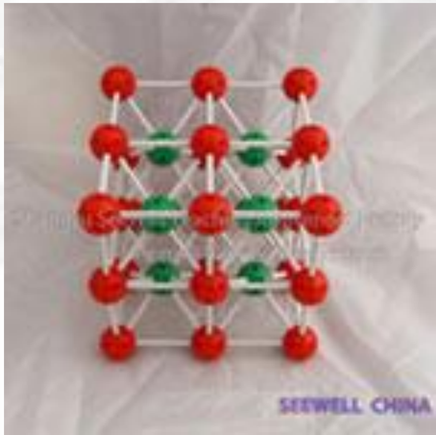


CHAPTER 3: CRYSTAL STRUCTURES

- Crystal Structure: Basic Definitions - lecture
- Calculation of material density – self-prep.
- Crystal Systems – lecture + self-prep.
- Introduction to Crystallography – lecture + self-prep.
- X-Ray Diffraction (XRD) – lecture

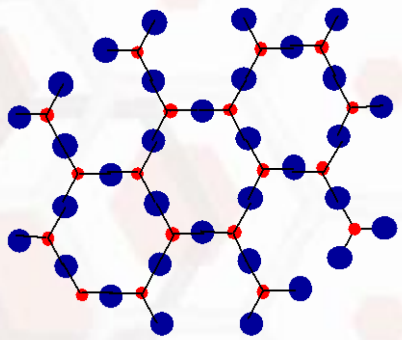


MATERIALS AND PACKING

Crystalline materials...

- atoms pack in periodic, 3D arrays
- typical of:

  -metals
  -many ceramics
  -some polymers



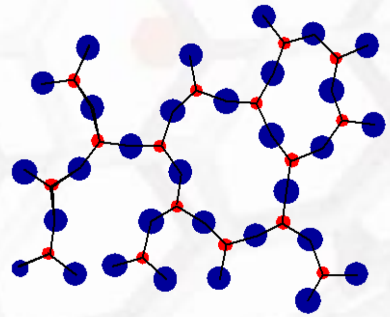
crystalline SiO_2

• Si • Oxygen

Non-crystalline materials...

- atoms have no periodic packing
- occurs for:

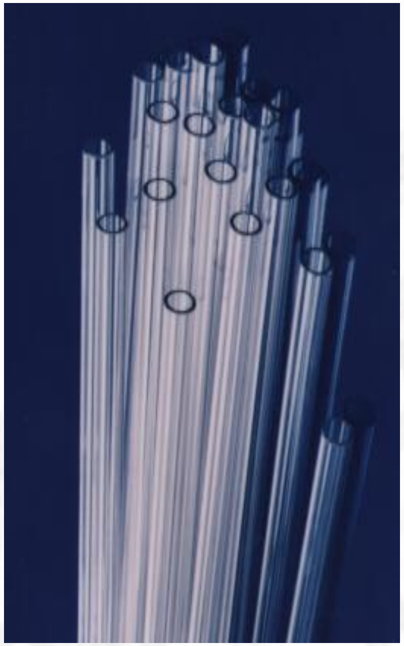
  -complex structures
  -rapid cooling



Non-crystalline SiO_2

"Amorphous" = Non-crystalline

Glass-Ceramics

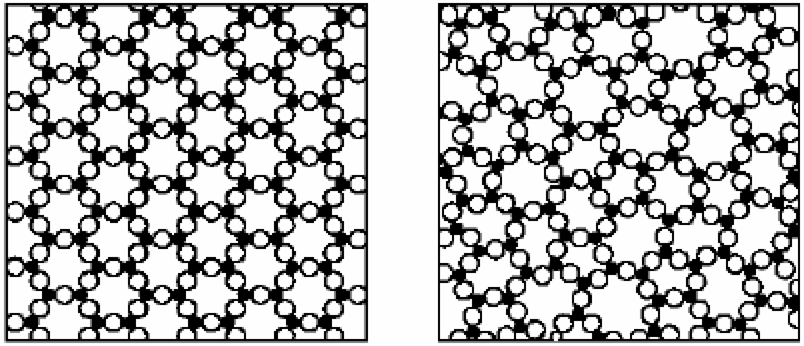


Quartz tubing is fabricated from beach sand

The lamp applications are shown in the GE product montage

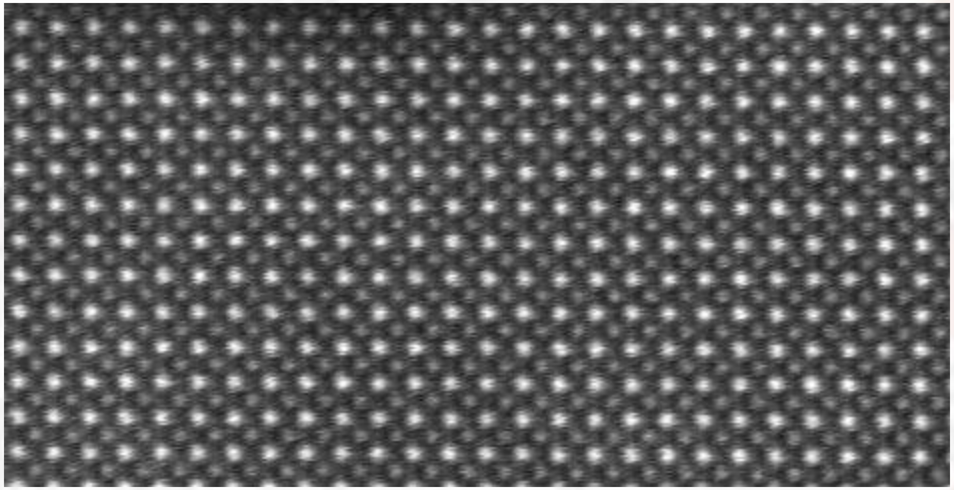
Highly thermal resistive ceramics

Ceramics Crystals: *atoms have long range periodic order*

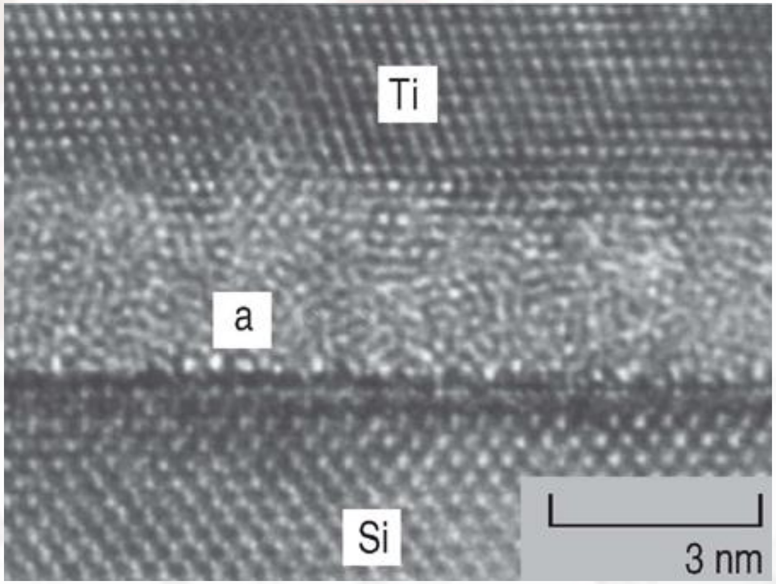


Glasses (non-crystalline): *atoms have short range order only (**amorphous**)*

Crystallography is the experimental science of the arrangement of atoms in solids. The word "crystallography" derives from the Greek words *crystallon* = cold drop / frozen drop, with its meaning extending to all solids with some degree of transparency, and *grapho* = write.

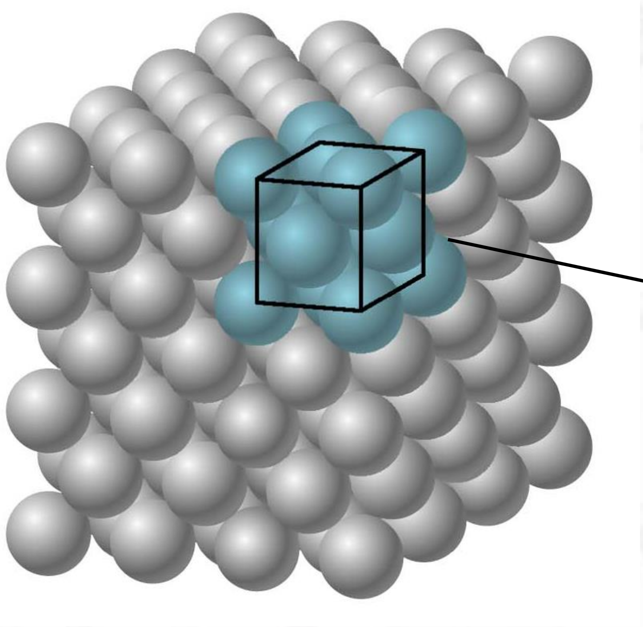


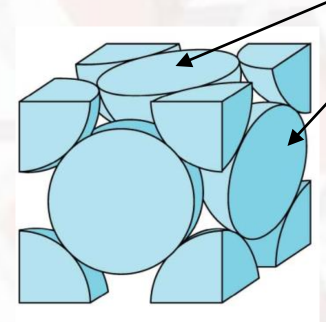
A **crystalline solid**: HRTEM image of strontium titanate. Brighter atoms are Sr and darker are Ti.



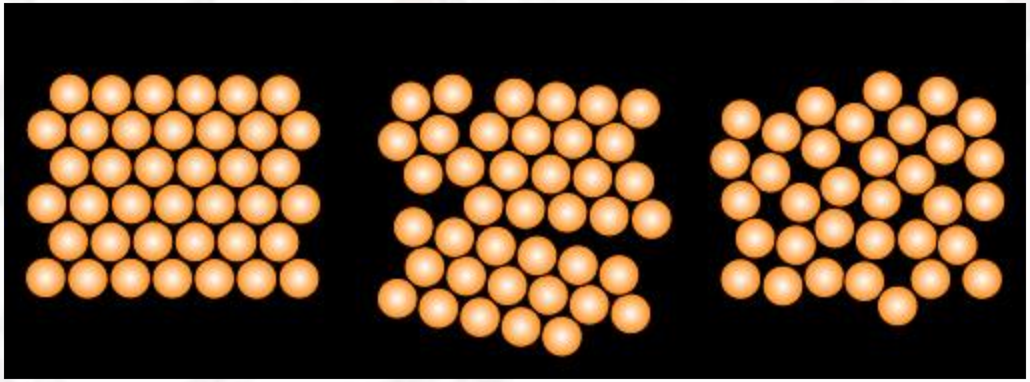
A TEM image of **amorphous interlayer** at the Ti/(001)Si interface in an as-deposited sample.

Crystal

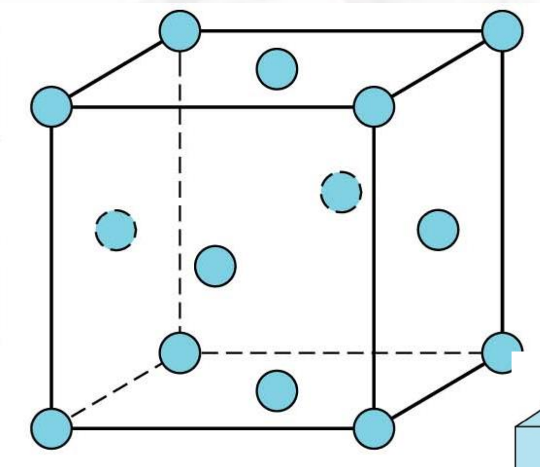




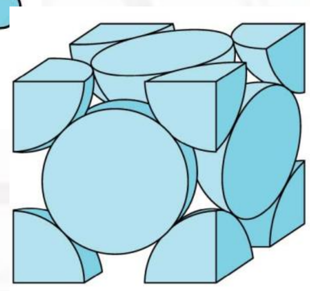
- **A CRYSTAL** is any solid material in which the component atoms are arranged in a ***definite patter*** and whose surface regularity reflects its ***internal symmetry***.

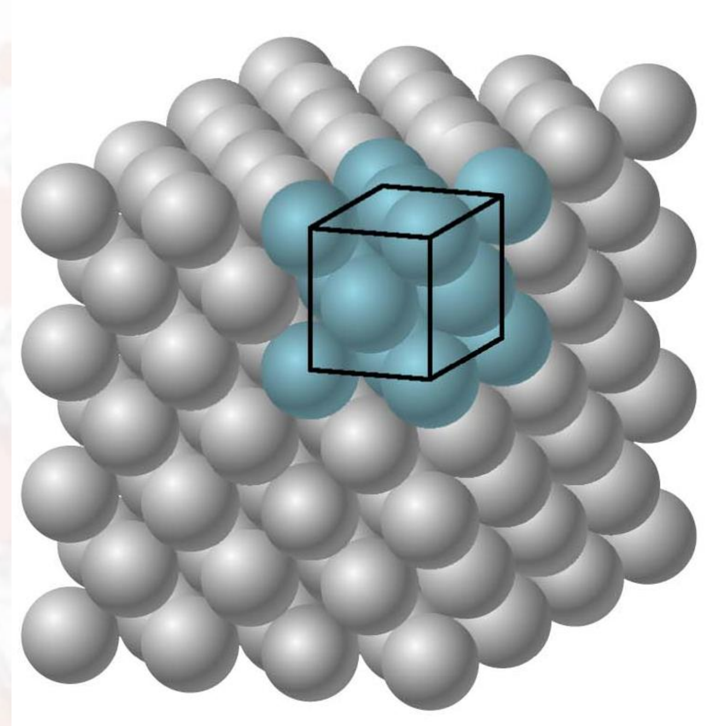


Unit Cell



Lattice points





Atomic **hard sphere** model

- Unit cell is the ***smallest*** unit of volume that permits **identical** cells to be stacked together ***to fill all space***.

- By ***repeating*** the pattern of the unit cell over and over in all directions, the entire **crystal** lattice can be constructed.

Crystal Systems: Possible Unit Cell Shapes

- Goal is to Quantitatively Describe

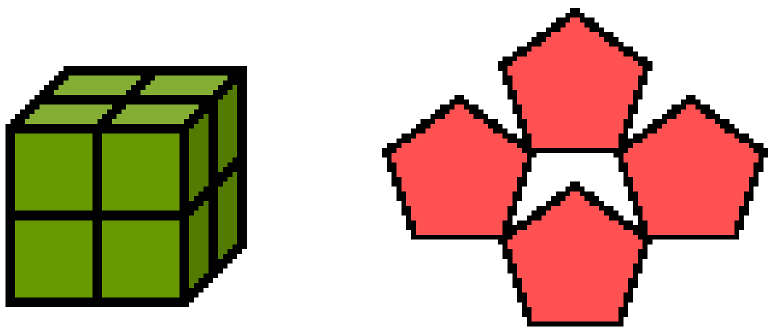
(a) ***Shape*** and ***Size*** of the Unit Cell (point symmetry)

(b) ***Location*** of the ***Lattice Points*** (translational symmetry)

- **What we will do ?**

For ***(a)*** to specify the **Crystal System** and the **Lattice Parameters**
For ***(b)*** to define the **"Bravais" Lattice**

Crystal Systems



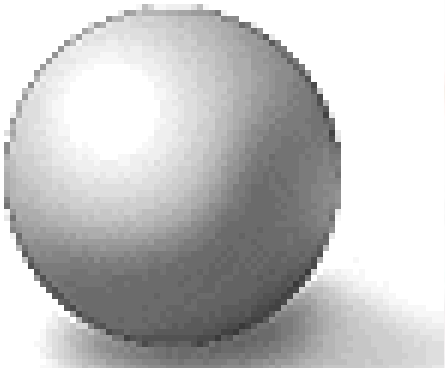
- Unit cells need to be able to "Stack" them to fill all space !!
- This puts ***restrictions*** on Unit Cell Shapes
- Cubes Work!
- Pentagons Don't!

Different types (but not ∞!!!!) of unit cell are possible, and they are classified based on their *level of symmetry*

Symmetry

Symmetry is a the set of mathematical rules that describe the shape of an object

Do you know that there is only ONE object in the geometrical universe with ***perfect symmetry***?



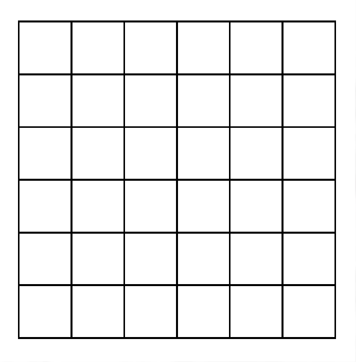
It is a **SPHERE**!!

Infinite ***planes*** of symmetry pass through its center, infinite ***rotational axes*** are present, and no matter how little or much you rotate it on any of its infinite number of axes, it appears the same!

A sphere is the ***HOLY GRAIL*** of symmetry!!

Crystal: Space Group

By definition crystal is a *periodic* arrangement of *repeating* “motifs”(e.g. atoms, ions). The ***symmetry*** of a periodic pattern of repeated motifs is the total set of symmetry operations allowed by that pattern



- Let us apply a ***rotation*** of 90 degrees about the center (**point**) of the pattern which is thought to be indefinitely extended. This pattern will be *unchanged* as a result of this operation, i.e. the operation maps the pattern onto itself.

- Also a linear shift (***translation***) of this pattern by a certain amount (e.g. by the length of a small square) results in that *same* pattern again.

- The total set of such symmetry operations, applicable to the pattern is the ***pattern's symmetry***, and is mathematically described by a so-called ***Space Group***

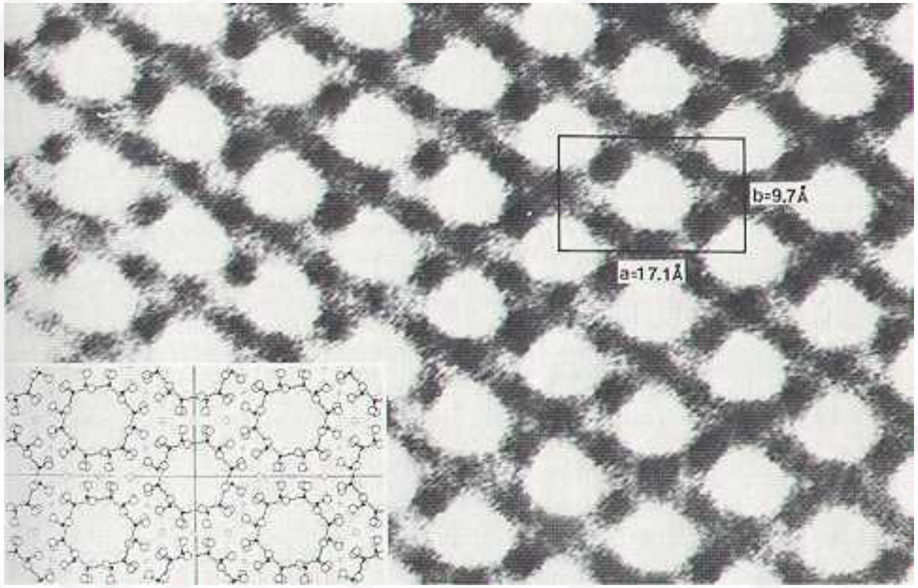
The ***Space Group of a Crystal*** describes the symmetry of that crystal, and as such it describes an important aspect of that crystal's internal structure

Translational Symmetry

A Space Group includes two main types of symmetries (i.e. symmetry operations)

(I) The ***Translational*** Symmetries, and (II) The **Point** Symmetries

Translations, i.e. executable shifting movements, proceeding along a straight line and on a certain specified distance, such that the operation does not result in any change of the shifted pattern.



High magnification structure image of the mineral Cordierite. The insert shows the idealized structure of Cordierite, as determined by X-ray diffraction techniques.
(Hurlbut & Klein, 1977, *Manual of Mineralogy*)

Typically the translational symmetries are ***macroscopically not visible*** because the translation lengths are in the order of Å.

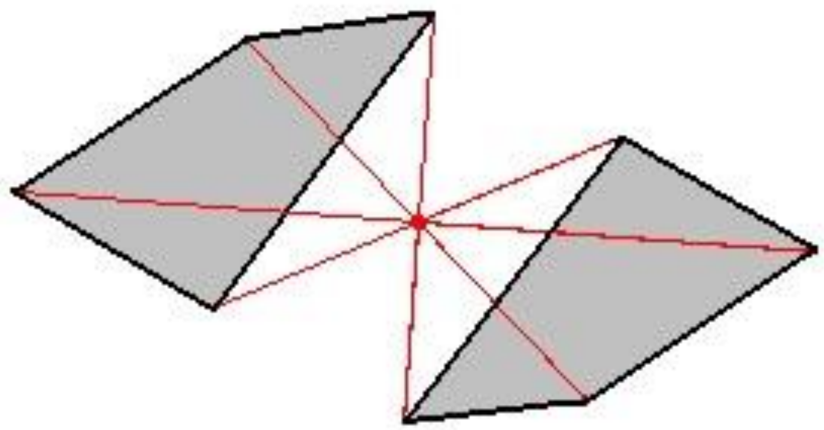
Point Symmetries

It is a ***macroscopically visible*** symmetry operations:
after it has been applied to the crystal at least ***one point*** remains where it was !!

These operations are **:**

- Reflection in a point (**inversion**) – ***Center of Symmetry***!
- Reflection in a plane or ***Mirror Symmetry*** !
- Rotation about an imaginary axis –***Rotational Symmetry***!
- Rotation-and-after-it-inversion or ***Roto-inversion***!

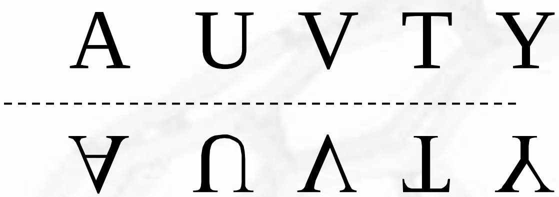
Center of Symmetry



Example:
The item, consists of two asymmetric faces:
the every part of the item can also be found on the opposite side of some point (center of symmetry!!) at the same distance !!

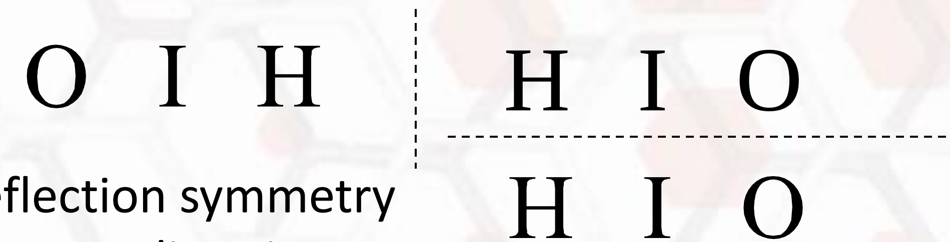
Reflection in a point or inversion!

Mirror Symmetry



Mirror Plane
vertical

Mirror Plane
horizontal



Reflection symmetry
in two directions

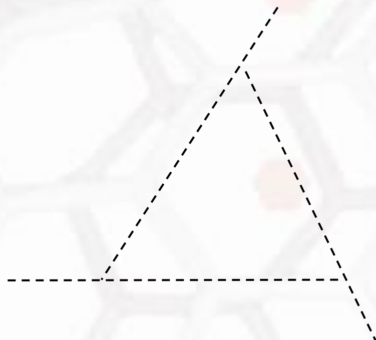
People and most vertebrates basically have mirror symmetry:
in biology it is called ***bilateral*** symmetry

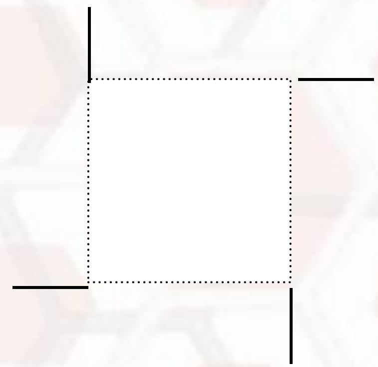
Rotational Symmetry

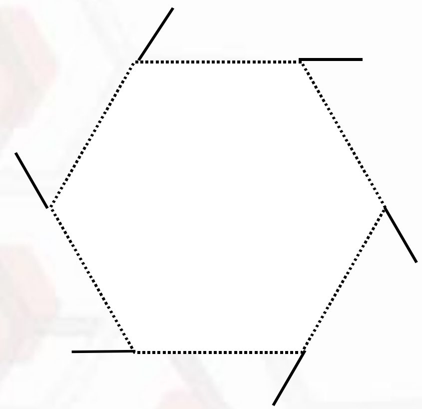
A point around we rotate – **symmetry axis**

6 6 / / / % / / / 99

Z S N







two-fold symmetry

three-fold symmetry

four-fold symmetry

six-fold symmetry

Figure looks the same n times in a 360° rotation.
n-fold symmetry!!

One-fold symmetry = No symmetry!!

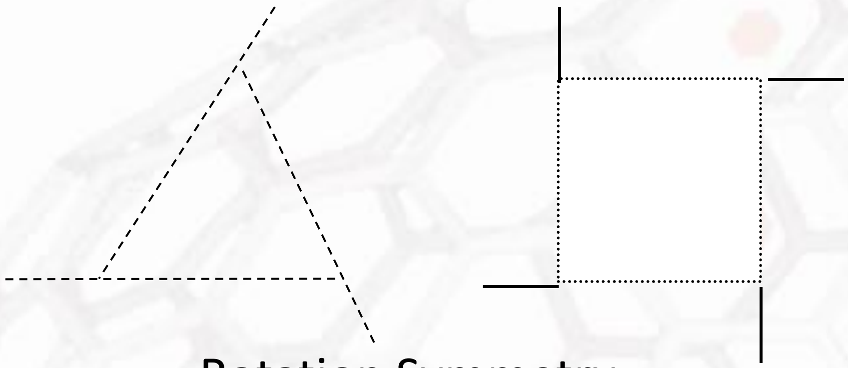
N-fold Roto-Inversion Symmetry

The object will be ***transformed into itself*** after the following **two step operation** (e.g. the 4-fold roto-inversion):

- a ***rotation*** of 90 degrees along the axis;

- followed by the ***inversion*** with respect to a point on the axis

Objects may have more than one kind of symmetry



Rotation Symmetry
without Reflection

Rotation Symmetry
and Reflection

O H I X

Mirror planes in two direction +
+ two-fold rotation symmetry

The Sets of Basic Symmetry Elements for Crystals

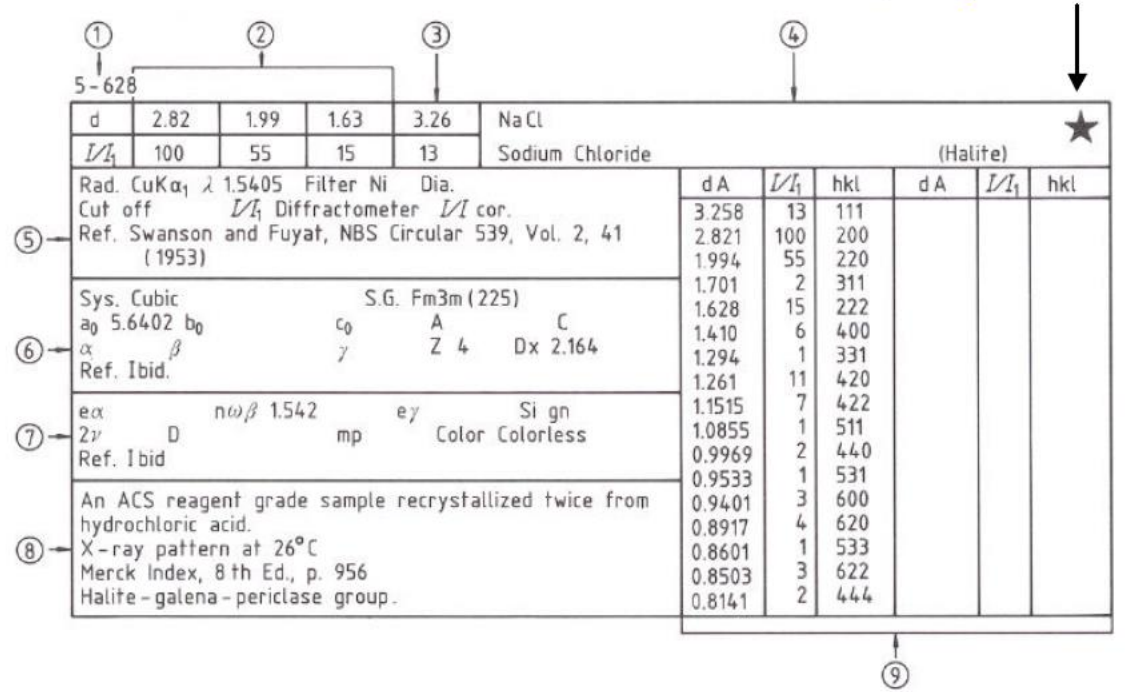
- 1 –fold rotation (rotation through 360 degrees); symbol: none
- 2 - fold rotation (rotation through 180 degrees); symbol: **2**
- 3 - fold rotation (rotation through 120 degrees); symbol: **3**
- 4- fold rotation (rotation through 90 degrees); symbol: **4**
- 6- fold rotation (rotation through 60 degrees); symbol: **6**

In the case of crystals the ***only*** above rotation axes can occur!!

- Mirror plane; symbol: **m**
- Center of Symmetry: **p**
- **4**-fold roto-inversion axis – ***unique element***!; symbol: **4***

JCPDS Card

Quality of data



5-628

d	2.82	1.99	1.63	3.26	NaCl
I/I_1	100	55	15	13	Sodium Chloride (Halite)

Rad. $CuK\alpha_1$ λ 1.5405 Filter Ni Dia.
Cut off I/I_1 Diffractometer I/I cor.
Ref. Swanson and Fuyat, NBS Circular 539, Vol. 2, 41 (1953)

Sys. Cubic S.G. Fm3m (225)
a_0 5.6402 b_0 c_0 A C
α β γ Z 4 Dx 2.164
Ref. Ibid.

$\epsilon\alpha$ $n\omega\beta$ 1.542 $\epsilon\gamma$ Si gn
$2V$ D mp Color Colorless
Ref. Ibid

An ACS reagent grade sample recrystallized twice from hydrochloric acid.
X-ray pattern at 26°C
Merck Index, 8 th Ed., p. 956
Halite - galena - periclase group.

d A	I/I_1	hkl	d A	I/I_1	hkl
3.258	13	111			
2.821	100	200			
1.994	55	220			
1.701	2	311			
1.628	15	222			
1.410	6	400			
1.294	1	331			
1.261	11	420			
1.1515	7	422			
1.0855	1	511			
0.9969	2	440			
0.9533	1	531			
0.9401	3	600			
0.8917	4	620			
0.8601	1	533			
0.8503	3	622			
0.8141	2	444			

1.file number 2.three strongest lines 3.lowest-angle line 4.chemical formula and name 5.data on diffraction method used 6.crystallographic data 7.optical and other data 8.data on specimen 9.data on diffraction pattern.

Joint Committee on Powder Diffraction Standards, JCPDS (1969)
Replaced by International Centre for Diffraction Data, ICDF (1978)

Crystal Classes

With all these point symmetries (i.e. Rotation, Reflection, and Roto-inversion) ***combinations*** can be made, which themselves are again cover operations, and this results in a ***total of 32 unique*** possibilities.

Thus all crystals can be classified in **32 CRYSTAL SYMMETRY CLASSES** according to their symmetry content, i.e. specific set of symmetry elements

For example:

- The **highest** symmetrical Cubic (Hexakisohedric) Class possess the following symmetry elements:

  Three 4-fold rotation axes.
  Four 3-fold rotation axes.
  Six 2-fold rotation axes.
  Three primary mirror planes.
  Six secondary mirror planes.
  Center of symmetry.

- The **lowest** symmetrical class Triclinic (Hemihedric) involves 1-fold rotation axis, thus ***no symmetry*** at all!!

The Crystal Systems

In turn these symmetry classes, because some of them show similarities among each other, are divided among the different ***Crystal Systems***.

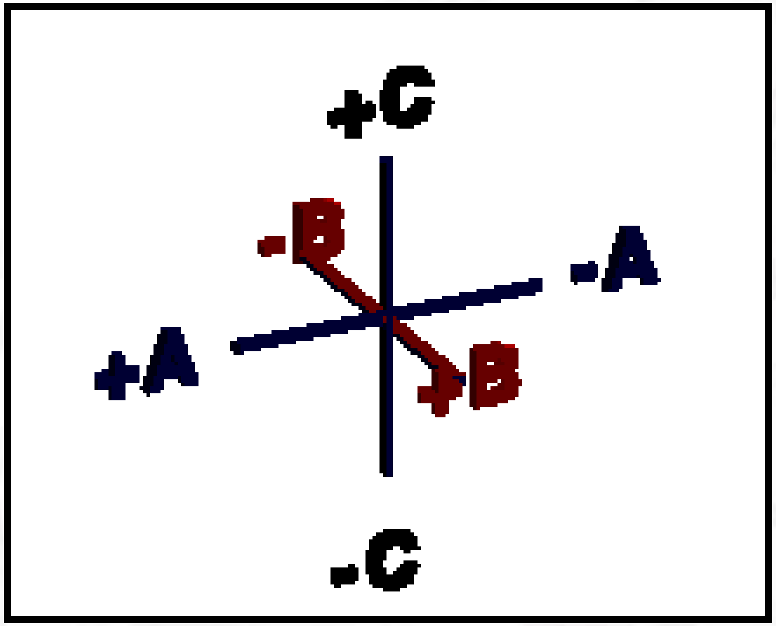
There are six Crystal System

1. **The CUBIC (also called Isometric system)**
2. **The TETRAGONAL system**
3. **The HEXAGONAL system**
4. **The ORTHORHOMBIC system**
5. **The MONOCLINIC system**
6. **The TRICLINIC system**

Decreasing symmetry

Every Crystal System involves a number of Crystal Classes.

CRYSTALLOGRAPHIC AXES



Refer to the axes in the order - a, b, c
The point of intersection of the three axes is called the **AXIAL CROSS**.

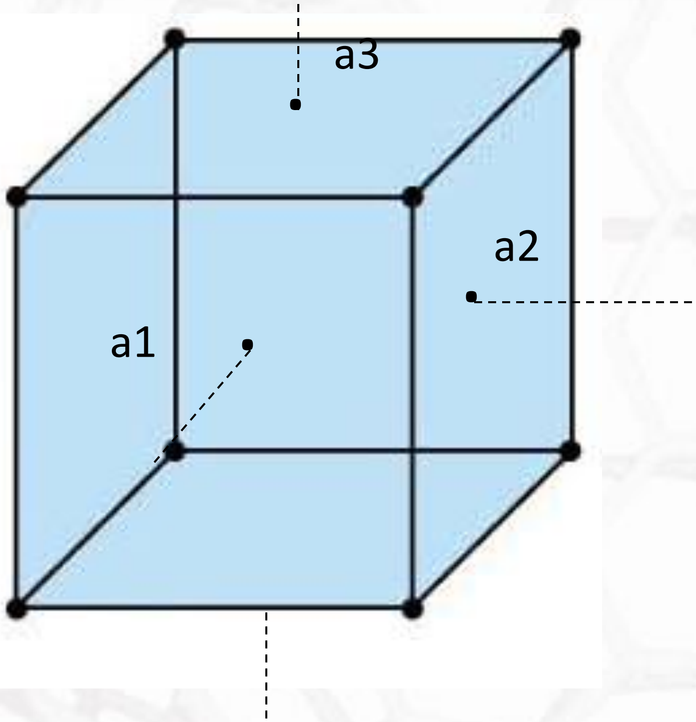
By using these crystallographic axes we can define six large groups or ***crystal systems*** that ***all crystal*** forms may be placed in

CUBIC (or ISOMETRIC) System -I

The three crystallographic axes are all equal in length and intersect at right angles to each other.

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

In general this system involves **6 classes of symmetries** and **15 crystal forms**



Cube - is one of the easiest to recognize and many minerals display it with little modification: pyrite, fluorite, perovskite, or halite cubes!

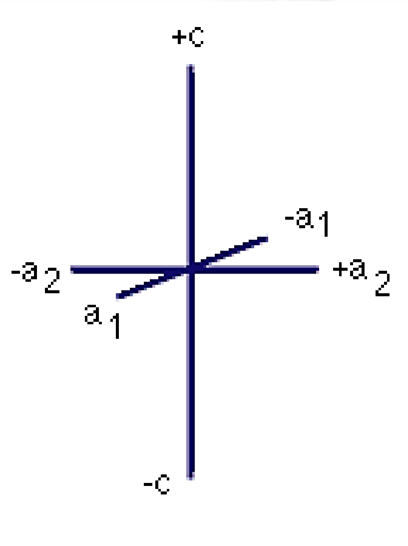
CUBIC (or ISOMETRIC)-II

If you glance on the ***Hexoctahedron***, which also belongs to this crystal system you will understand why crystal forms in the isometric system have the highest degree of **SYMMETRY**, when compared to all the other crystal systems.

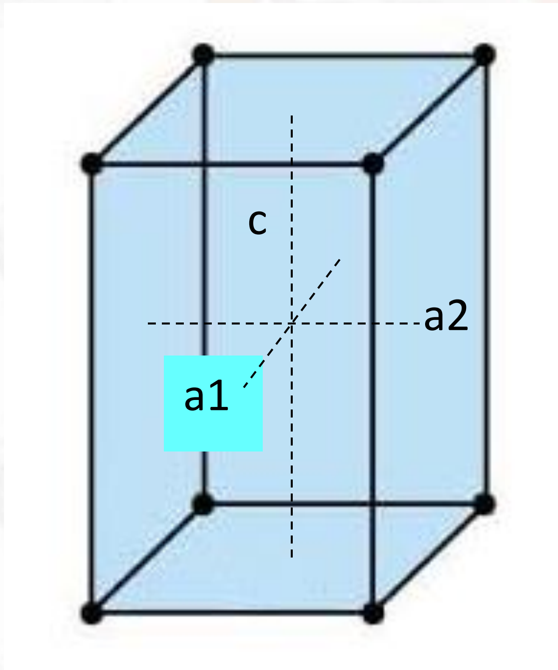
Compare with Sphere!!

TETRAGONAL System

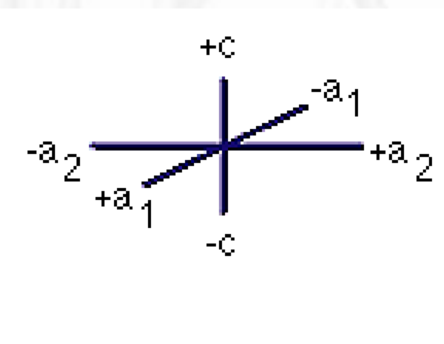
Three axes, all at right angles, two of which are equal in length (a and b) and one (c) which is different in length (shorter or longer).



$a = b \neq c \quad \alpha=\beta=\gamma=90^\circ$



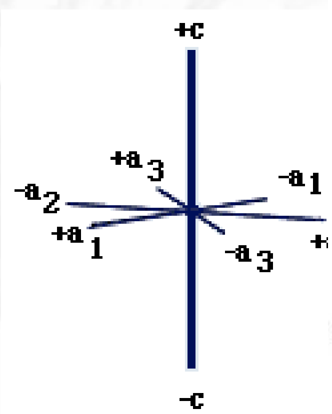
A **tetragonal prism** is one of the **9 forms** in this crystallographic system with **7 classes of symmetry**

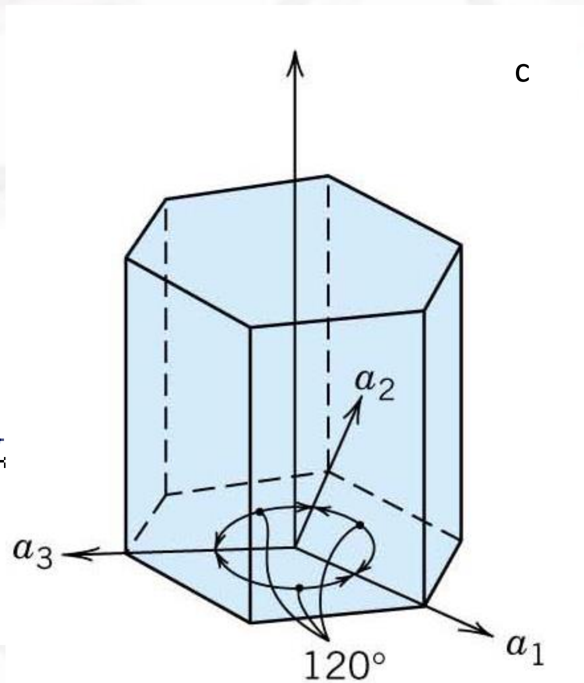


Note: If c was equal in length to a or b, then we would be in the cubic system!

HEXAGONAL System

Four axes! Three of the axes fall in the same plane and intersect at the axial cross at ***120°*** . These 3 axes, labeled a1, a2, and a3, are the ***same length***. The fourth axis, c, may be ***longer*** or ***shorter*** than the a axes set. The **c** axis also passes through the intersection of the **a** axes set at ***right angle*** to the plane formed by the a set.





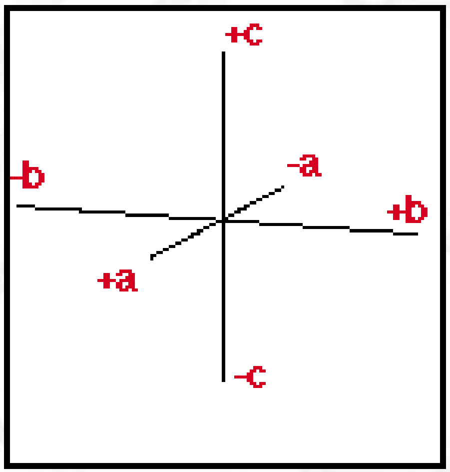
Example:
Normal ***prism***

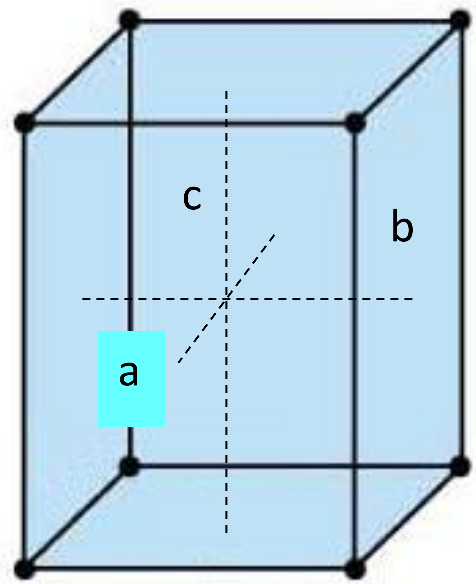
Hexagonal division:
nine forms
7 classes 6-fold symmetry
Trigonal division:
six forms
5 classes 3-fold symmetry
In some classifications:
Rhombohedrial Crystal System

ORTHOROMBIC System

Three axes, all at right angles, all three have different length.

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





Five forms

3 symmetry classes:

2-fold axis of rotation

And/or mirror symmetry

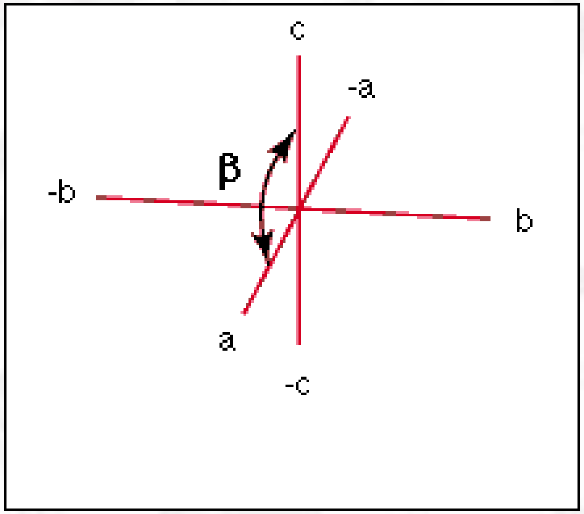
A pinacoid, also called the parallelohedron, is one of the forms in this crystallographic system

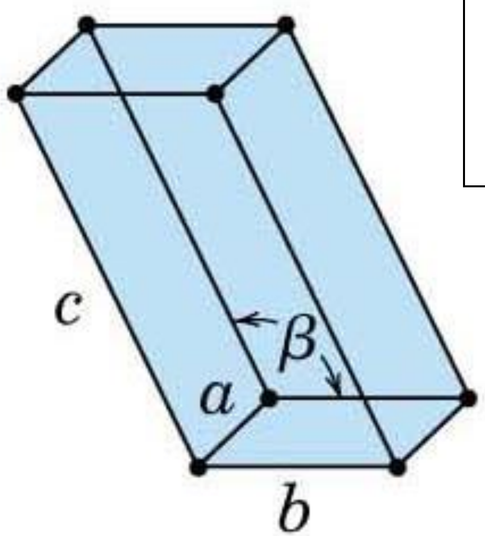
Note: If any axis was of equal length to any other, then we would be in the tetragonal system!

MONOCLINIC System

Three axes, all unequal in length, two of which (a and c) intersect at an oblique angle (not 90 degrees), the third axis (b) is perpendicular to the other two axes.

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





Three forms
3 symmetry classes:
2-fold axis of rotation
And/or mirror symmetry

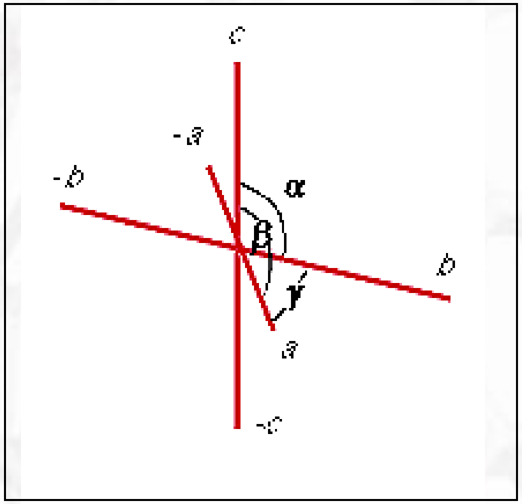
Example:
A ***monoclinic prism***

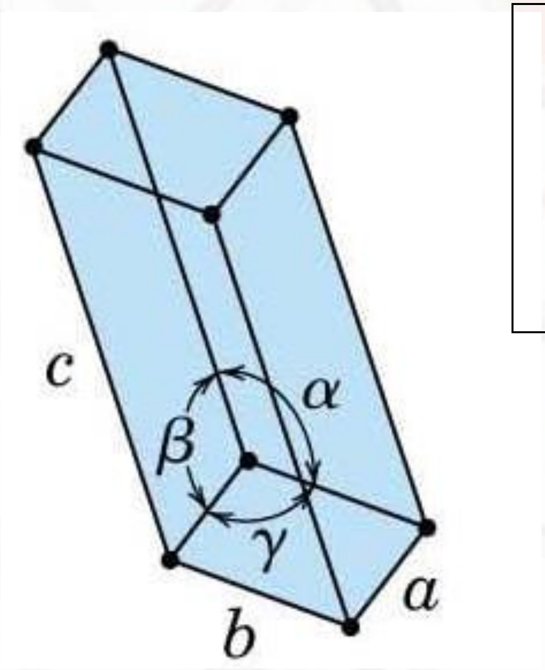
Note: If a and c crossed at 90 degrees, then we would be in the orthorhombic system!

TRICLINIC System

The three axes are all unequal in length and intersect at three different angles (any angle but 90 degrees).

$$a \neq b \neq c \quad \alpha \neq \beta \neq \gamma \neq 90^\circ$$





Two forms
2 symmetry classes:
Zero or 1-fold axis
symmetry!!

Example:
Triclinic ***Pinacoid***

Note: If any two axes crossed at 90 degrees, then we would be describing a monoclinic crystal!

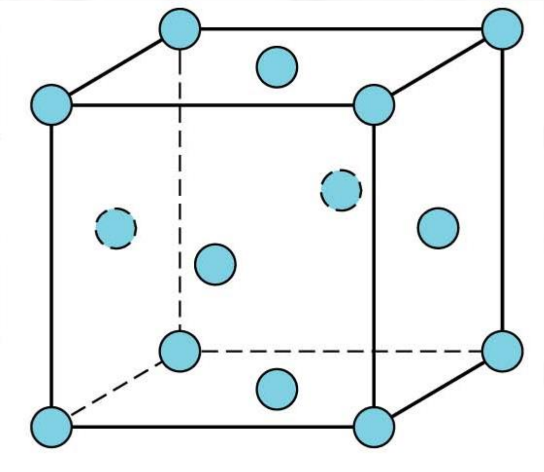
The Crystal Systems

1. The CUBIC (also called Isometric system)
2. The TETRAGONAL system
3. The HEXAGONAL system
4. The ORTHORHOMBIC system
5. The MONOCLINIC system
6. The TRICLINIC system

Decreasing symmetry

Bravais Lattices

- By means of unit cells we managed to reduce all possible crystal structures to a relatively small numbers of basic unit cell geometries.
- Now let us consider the issue how atoms (viewed as hard spheres) can be stacked together ***within a given unit cell.***

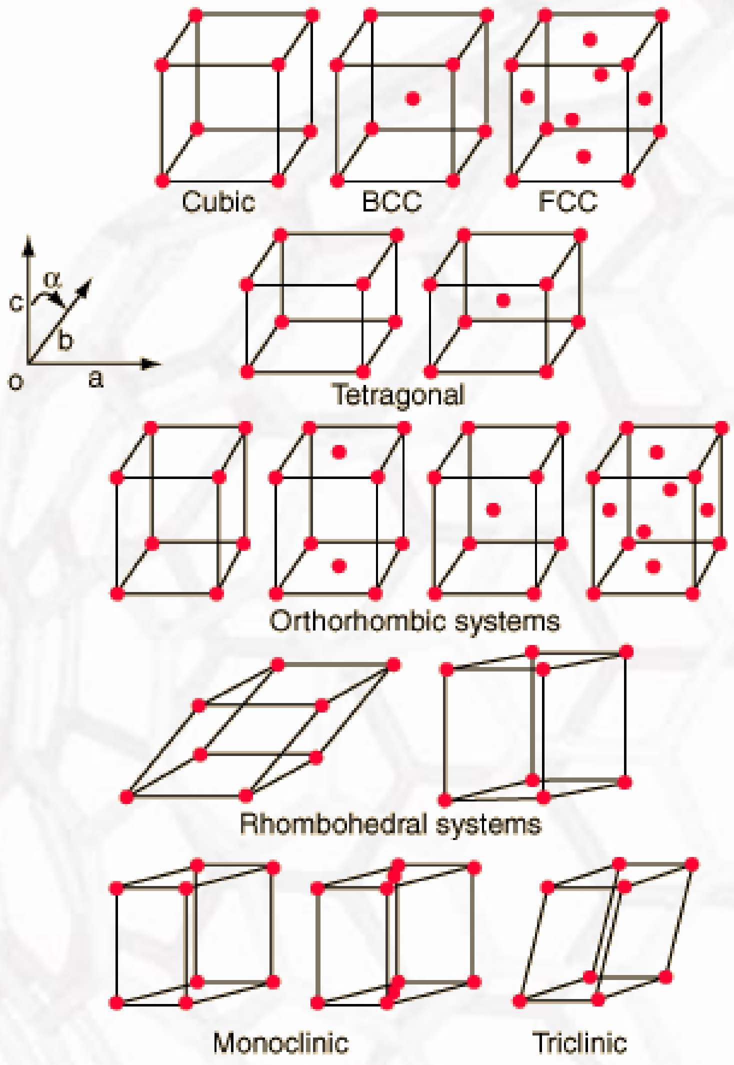


Lattice points are theoretical points arranged periodically in 3-D space, rather than actual atoms

- And again there is a limited number of possibilities, referred to as ***Bravais lattice***

Lattice points

The 14 Bravais Lattices



Where Can I Put the Lattice Points?

- The French scientist August Bravais, demonstrated in 1850 that only these ***14 types*** of unit cells are compatible with the orderly arrangements of atoms found in crystals.

- These three-dimensional configurations of points used to describe the orderly arrangement of atoms in a crystal.

- Each point represents one or more atoms in the actual crystal, and if the points are connected by lines, a crystal lattice is formed.

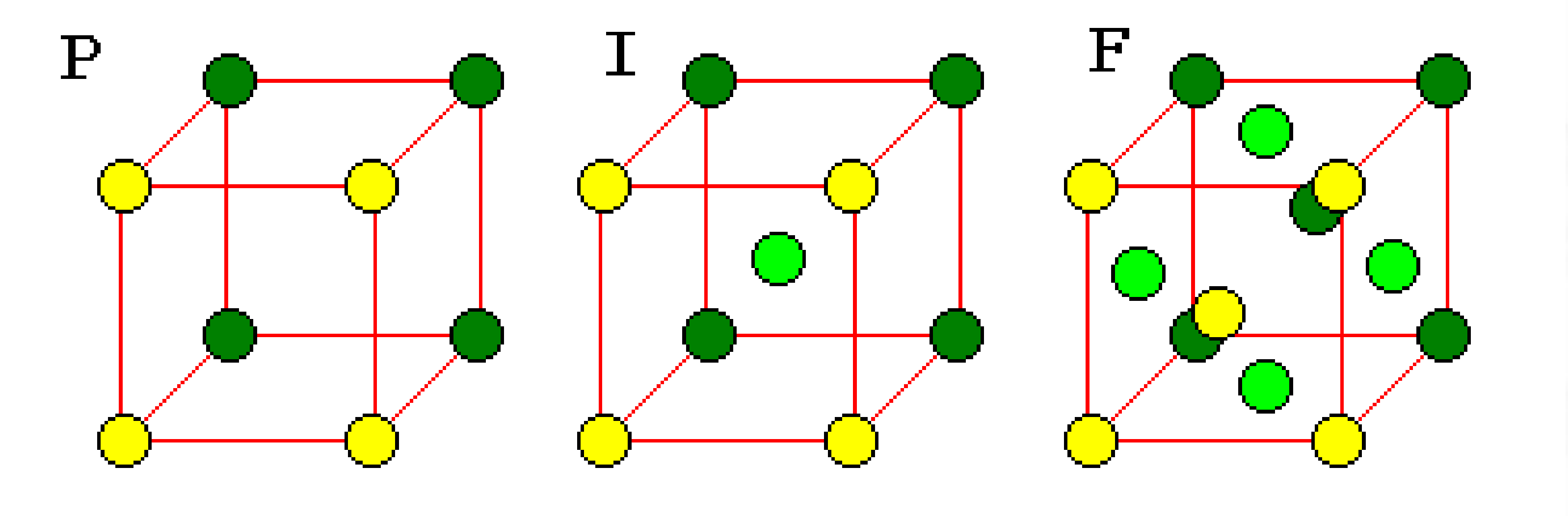
Bravais Lattices

Crystal System	Bravais Type	External Minimum Symmetry	Unit Cell Properties
Triclinic	P	None	a, b, c, al, be, ga,
Monoclinic	P, C	One 2-fold axis	a, b, c, 90, be, 90
Orthorhombic	P, I, F	Three perpendicular 2-folds	a, b, c, 90, 90, 90
Tetragonal	P, I	One 4-fold axis, parallel c	a, a, c, 90, 90, 90
Trigonal	P, R	One 3-fold axis	a, a, c, 90, 90, 120
Hexagonal	P	One 6-fold axis	a, a, c, 90, 90, 120
Cubic	P, F, I	Four 3-folds along space diagonal	a, a, a, 90, 90, 90

Symbols

- P - Primitive: simple unit cell
- F - Face-centered: additional point in the center of each face
- I - Body-centered: additional point in the center of the cell
- C – Base-Centered: additional point in the center of each end
- R - Rhombohedral: Hexagonal class only

Isometric Cells



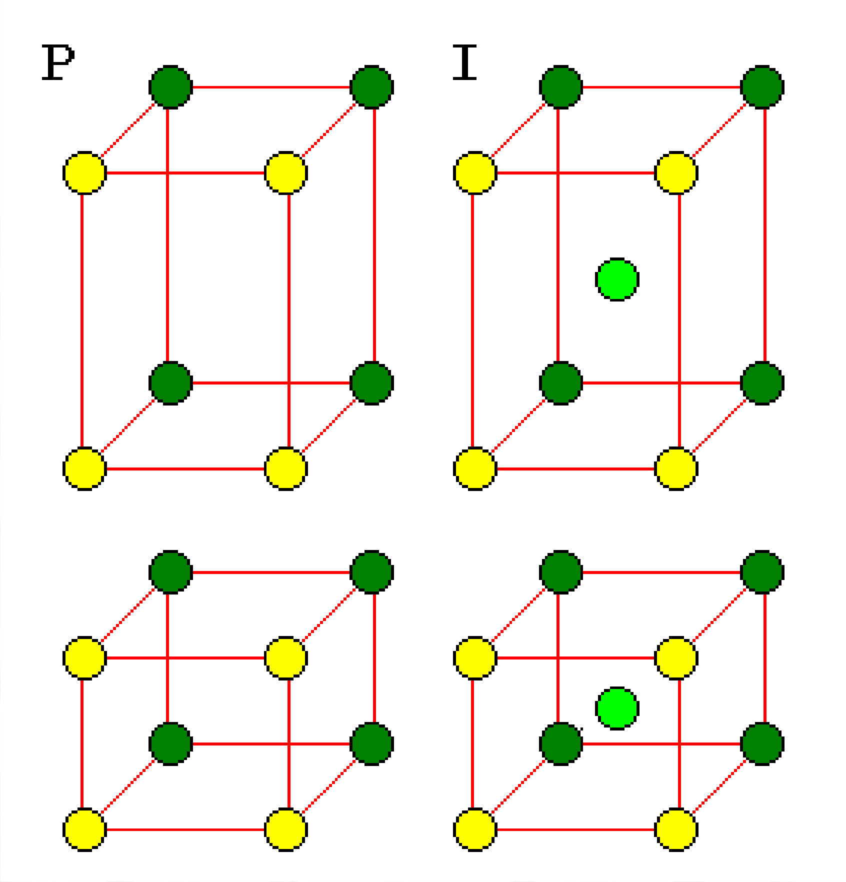
Simple cubic (P)

Body Centered Cubic (BCC; I)

Face Centered Cubic (FCC; F)

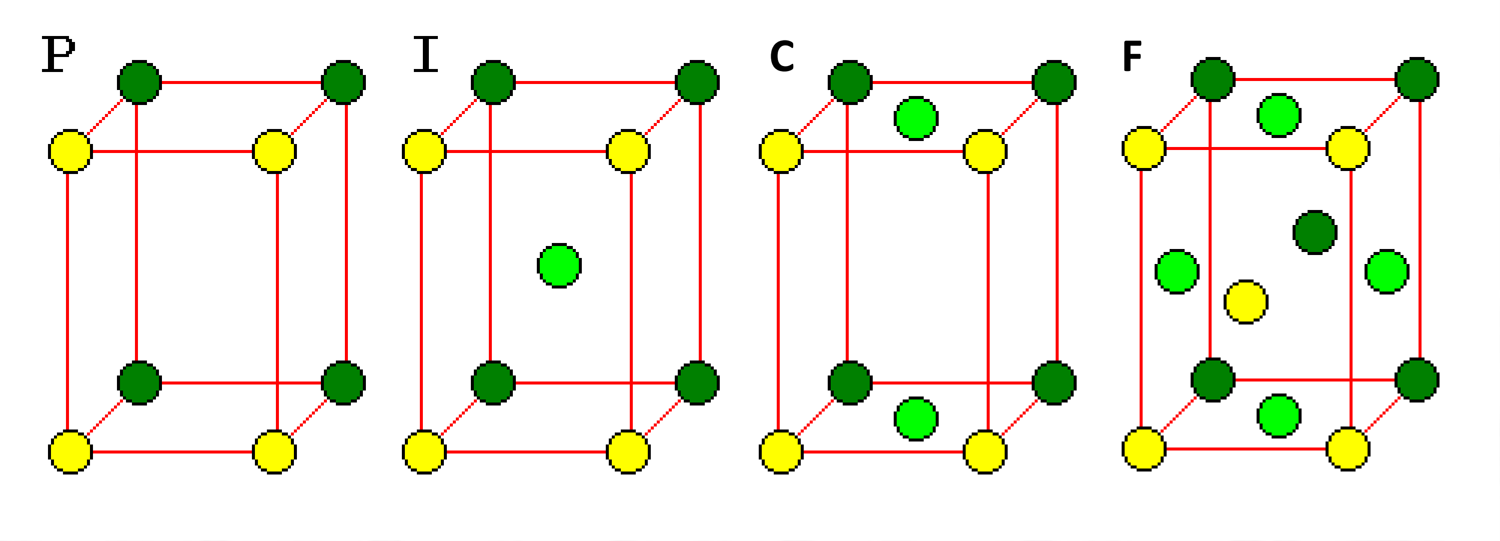
• The F cell is very important because it is the pattern for cubic closest packing. There is no centered (C) cell because such a cell would not have cubic symmetry.

Tetragonal Cells

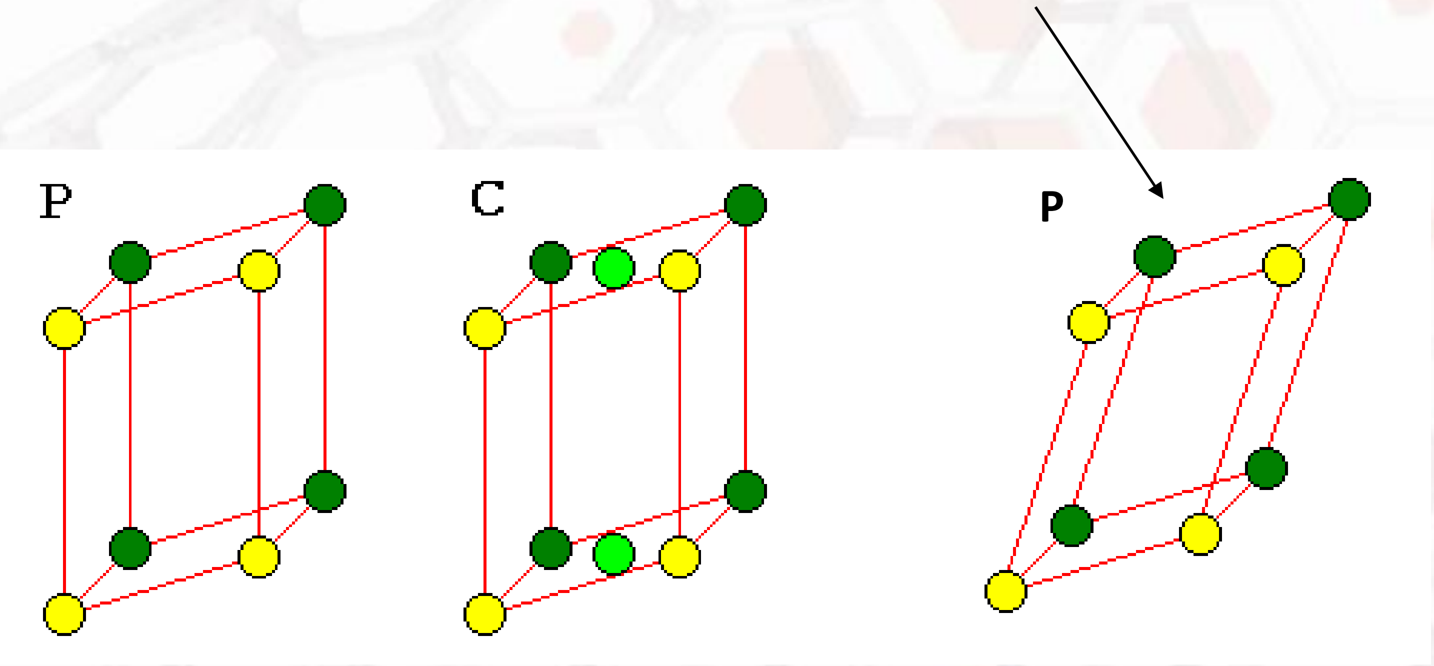


- A **C** cell would simply be a **P** cell with a smaller cross-section.
- While an F cell would reduce to a network of **I** cells.

Orthorhombic Cells

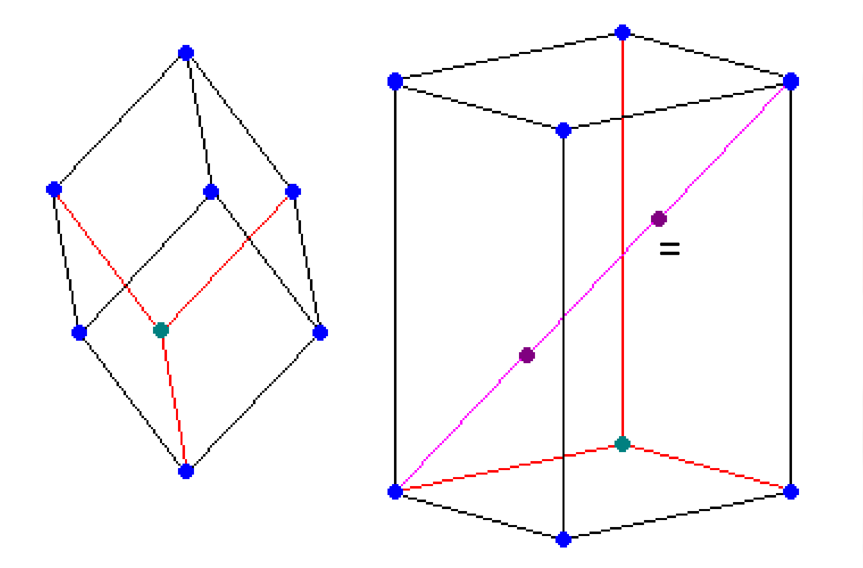


Monoclinic and Triclinic Cells



Monoclinic F or I cells could also be represented as C cells.
Any other triclinic cell can also be represented as a P cell.

Trigonal Cells



R
(Rhombohedral)

- The R cell is unique to hexagonal crystals. The two interior points divide the long diagonal of the cell in thirds. This is the only Bravais lattice with more than one interior point.
- A Rhombohedron can be thought of as a cube distorted along one of its diagonals.

Conclusion: The Crystal Systems

Decreasing symmetry

1. The CUBIC
2. The TETRAGONAL
3. The HEXAGONAL
4. The ORTHORHOMBIC
5. The MONOCLINIC
6. The TRICLINIC

Name	# Bravais lattice	Conditions
Triclinic	1	$a1 \neq a2 \neq a3$ $\alpha \neq \beta \neq \gamma$
Monoclinic	2	$a1 \neq a2 \neq a3$ $\alpha=\beta=90° \neq \gamma$
Orthorhombic	1	$a1 \neq a2 \neq a3$ $\alpha=\beta=\gamma=90°$
Hexagonal	1	$a1=a2 \neq a3$ $\alpha=\beta=90°$ $\gamma=120°$
Trigonal (Rhormohedral)	4	$\alpha=\beta=\gamma=90°$ $\alpha=\beta=\gamma \neq 90°$
Tetragonal	2	$a1=a2 \neq a3$ $\alpha=\beta=\gamma=90°$
Cubic	3	$a1=a2=a3$ $\alpha=\beta=\gamma=90°$