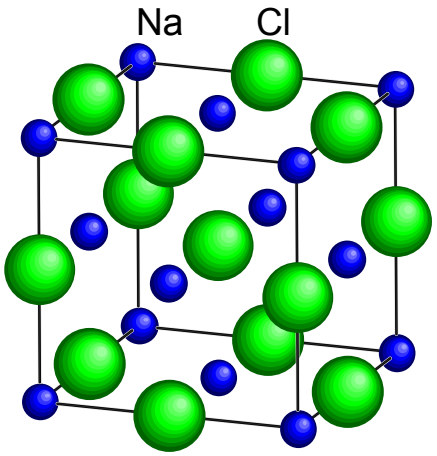
Analytical Methods for Materials

Lesson 7
Crystal Geometry and Crystallography, Part 1

Suggested Reading

- Chapters 2 and 6 in Waseda et al.

Salt crystals



http://healthfreedoms.org/2009/05/24/table-salt-vs-unrefined-sea-salt-a-primer/

Shapes of crystals can give us a clue about atomic arrangement

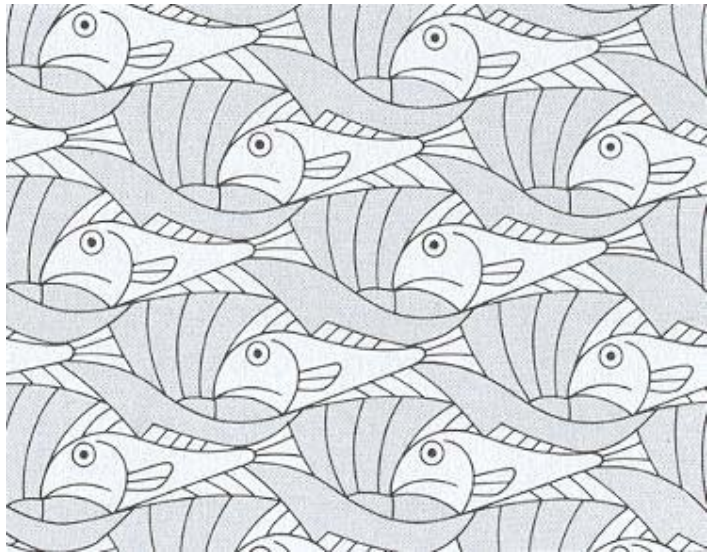
What is a crystal?

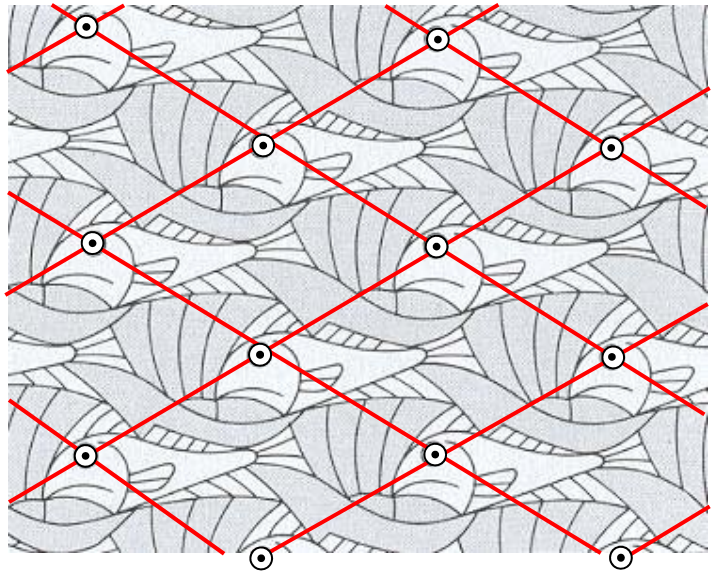
- Solids where atoms are arranged in *periodic* (i.e., repeating, symmetric, etc.) patterns.

What is symmetry?

- Describes how a ‘pattern’ repeats within a crystal.

Crystal Structure = Lattice + Motif [Basis]





P1

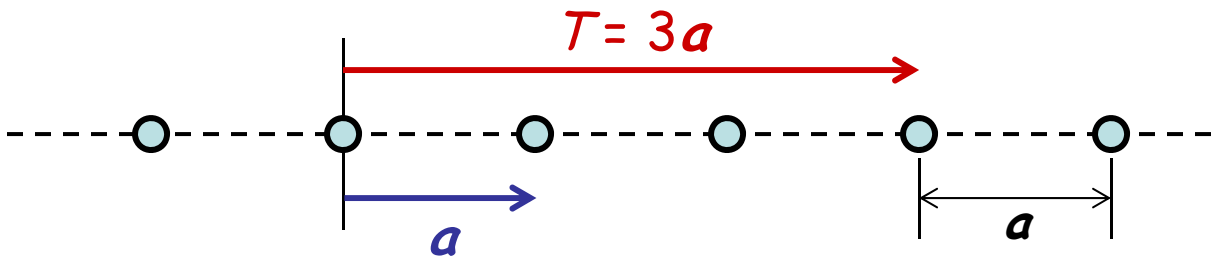
Complex Motif

From website: http://www.metafysica.nl/turing/promorph_crystals_preparation_3.html

A lattice must be symmetric!

Motifs must be arranged symmetrically!

One-Dimensional Lattice



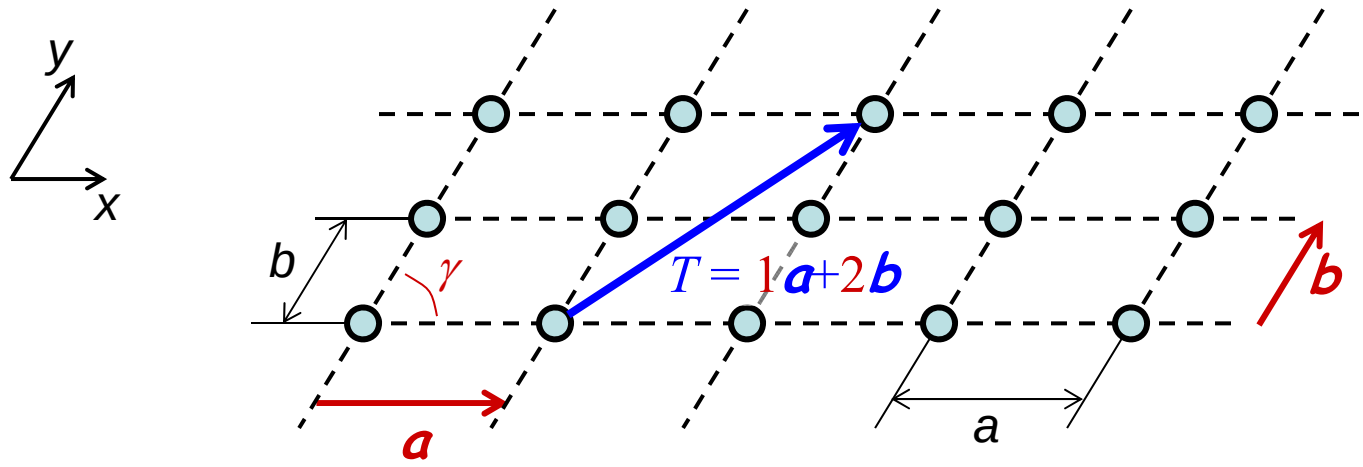
► Lattice symmetry implies that each lattice point must have identical surroundings (i.e., the same "environment").

- In a given direction, all *lattice points* must be separated by an identical distance, $\boldsymbol{a}$ (this basis vector is a *lattice parameter*).

- In a 1D lattice, a translation of $n\boldsymbol{a}$ from one lattice point to another, where n is an integer, brings you to an "identical" lattice point.

$$T = n\boldsymbol{a}$$

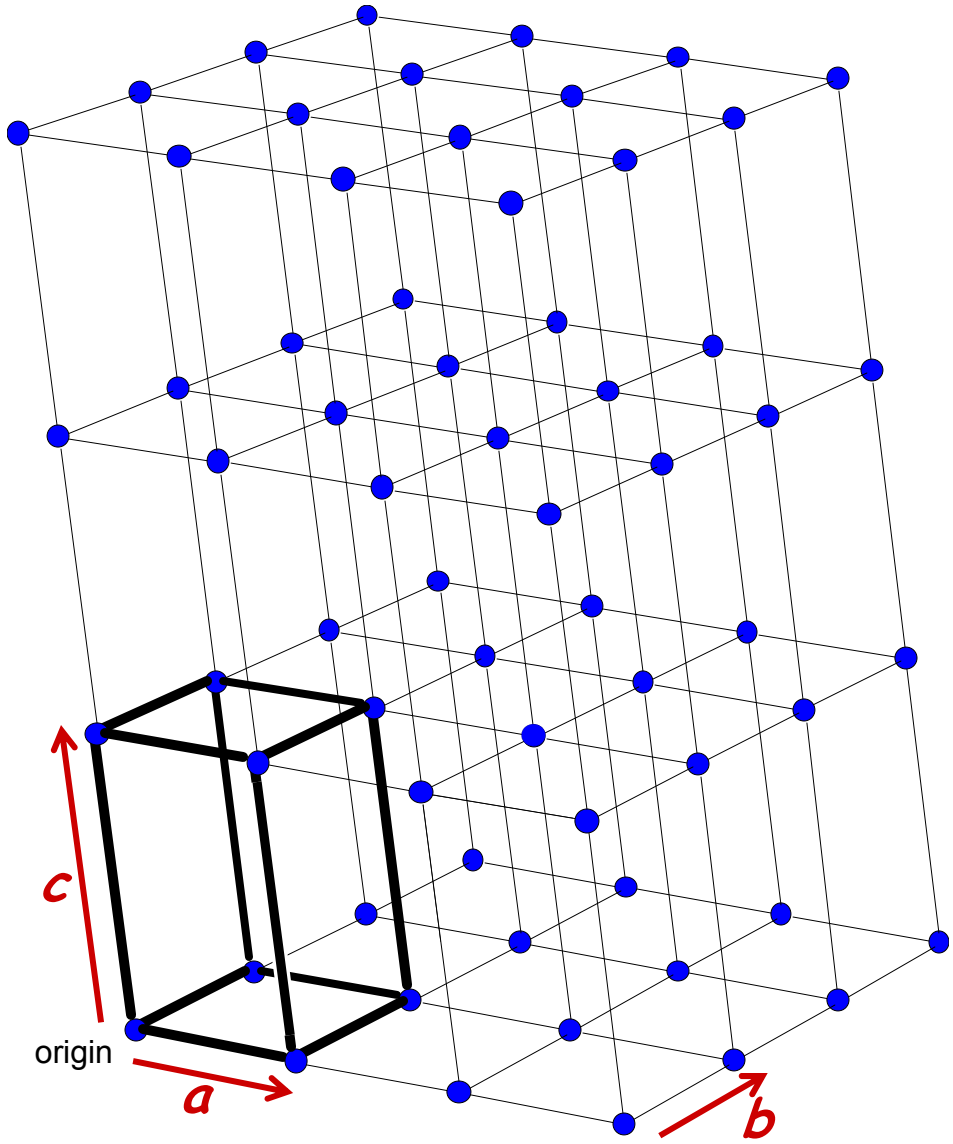
Two-Dimensional Lattice



- There are two non-collinear basis vectors ($\boldsymbol{a}$ and $\boldsymbol{b}$).
- A translation of $n\boldsymbol{a} + p\boldsymbol{b}$ from one lattice point to another must bring you to an 'equivalent' lattice point.
- The *interaxial angle* γ defines the relationship between the two basis vectors.

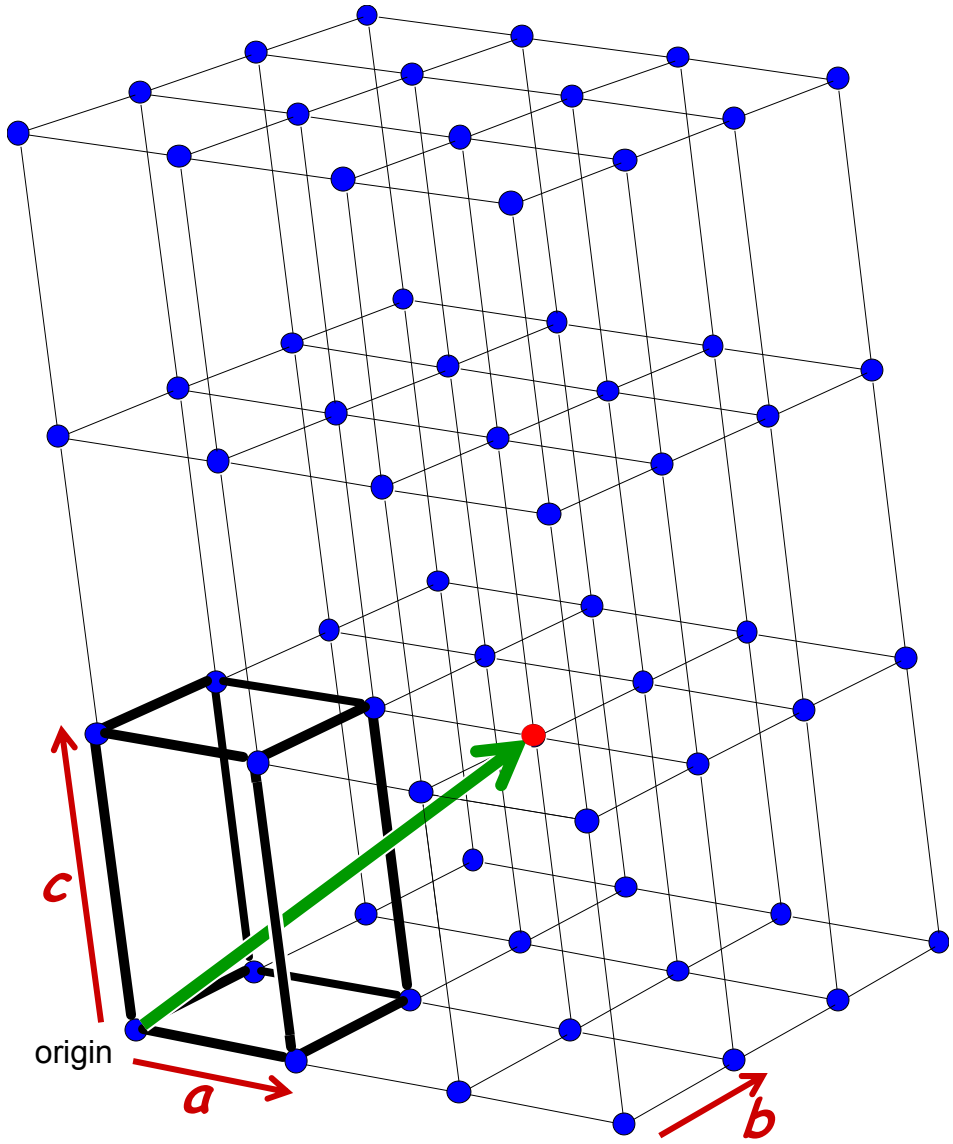
$$T = n\boldsymbol{a} + p\boldsymbol{b}$$

Three-Dimensional Lattice



- There are 3 non-collinear basis vectors and 3 interaxial angles.
- All points can be defined by a series of vectors:
  - $T = n\mathbf{a} + p\mathbf{b} + q\mathbf{c}$

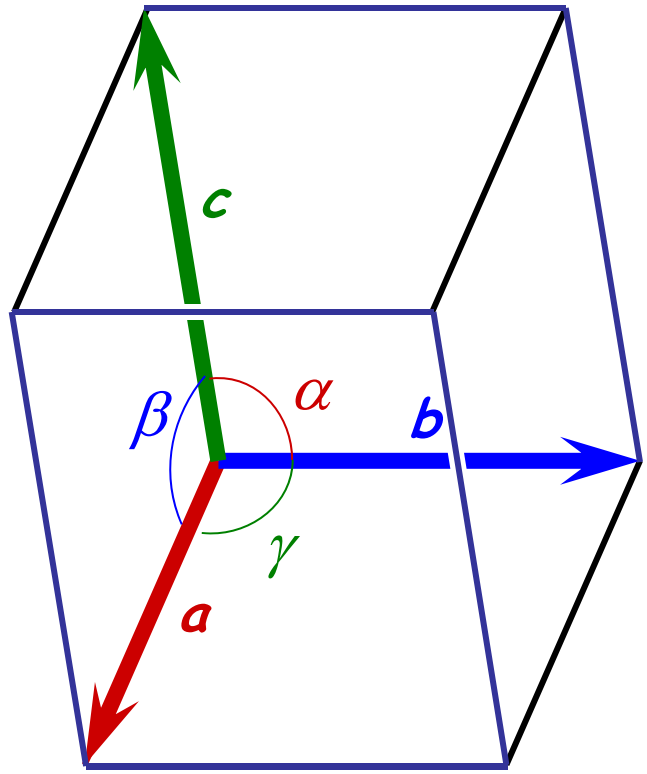
Three-Dimensional Lattice$^{cont'd}$



- The Basis vectors define the 'shape' of the crystal.
- The smallest repeating unit formed by combining the basis vectors is called a *unit cell*.
- A unit cell retains all characteristics of the lattice.

Lattice Parameters

The basis vectors are not necessarily orthogonal.



Axis →	*a*	*b*	*c*	*a*
Inter-axial angle →		γ	α	β

Unit Cell Shapes

- Unit cells in crystals have specific shapes.
- We call the shapes *crystal systems*[*].
- They are based upon:
  1. Highest symmetry
  2. Consistency with past convention
  3. Minimized unit cell volume
  4. Satisfaction of minimal symmetry requirements.
- All crystal structures evolve from crystal systems.

[*] A set of reference axes used to define the geometry of crystal and crystal structures

Crystal Systems

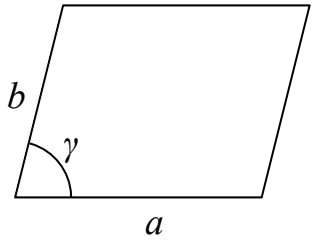
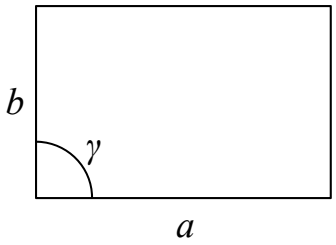
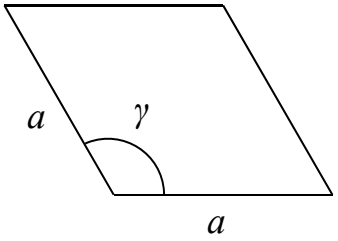
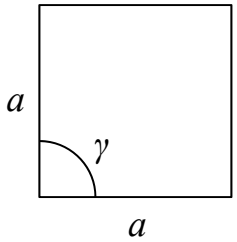
- In 2D there are only four (4).
  1. Oblique
  2. Rectangular
  3. Hexagonal
  4. Square

- In 3D there are only seven (7).
  1. Triclinic (anorthic)
  2. Monoclinic
  3. Hexagonal
  4. Rhombohedral (trigonal)
  5. Orthorhombic
  6. Tetragonal
  7. Cubic

The crystal systems are the only possible shapes for unit cells

With these shapes, you can fill all available space and leave no voids!

2D Crystal Systems

$a \neq b$ $\gamma \neq 90°$	**OBLIQUE PARALLELOGRAM**	
$a \neq b$ $\gamma = 90°$	**RECTANGLE**	
$a = b$ $\gamma = 120°$	**HEXAGONAL**	
$a = b$ $\gamma = 90°$	**SQUARE**	

3D Crystal Systems

Crystal System	Axial Relationships	Interaxial Angles
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°; \gamma = 120°$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$
Rhombohedral (Trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90° \neq \beta$
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$

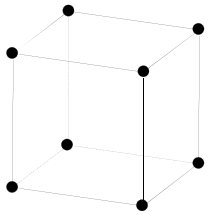
7 crystal systems

The mineral images are from various sites on the internet

Cubic

$a = b = c$

$\alpha = \beta = \gamma = 90°$

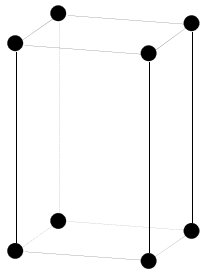


fluorite

Tetragonal

$a = b \neq c$

$\alpha = \beta = \gamma = 90°$

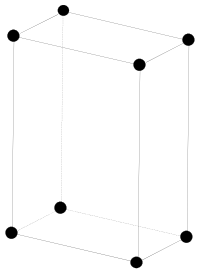


rutile

Orthorhombic

$a \neq b \neq c$

$\alpha = \beta = \gamma = 90°$

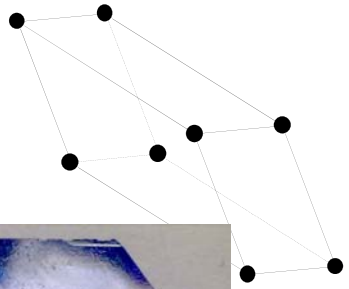


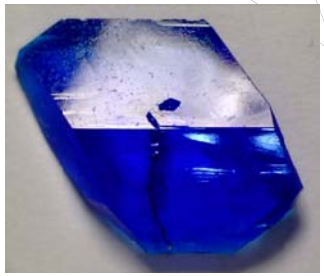
barite

Triclinic

$a \neq b \neq c$

$\alpha \neq \beta \neq \gamma \neq 90°$



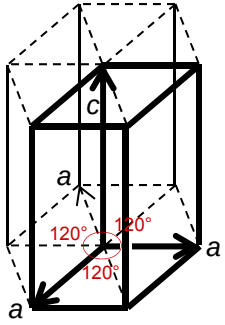


copper sulfate pentahydrate

Hexagonal

$a = b \neq c$

$\alpha = \beta = 90°; \gamma = 120°$

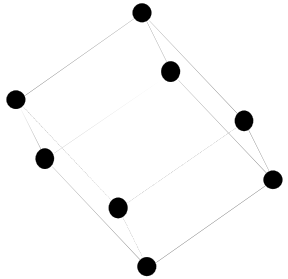


corundum

Rhombohedral

$a = b = c$

$\alpha = \beta = \gamma \neq 90°$

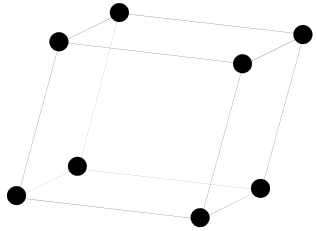


purple fluorite

Monoclinic

$a \neq b \neq c$

$\alpha = \gamma = 90° \neq \beta$



orthoclase

Keep in mind

- Crystal shape reveals the underlying symmetry of crystal.

- Must place lattice points on shape to build up a symmetric lattice.

All lattice points must be identical

What defines lattices and unit cells?

- Symmetry limits the number of possibilities.
- Crystal lattices must exhibit a specific minimal amount of symmetry.
- Each crystal system has a certain symmetry (lattice points have specific arrangements).

Symmetry Operators

- Motions that allow a pattern to be transformed from an initial position to a final position such that the initial and final patterns are indistinguishable.

1. Translation
2. Reflection
3. Rotation
4. Inversion (center of symmetry)
5. Roto-inversion (inversion axis)
6. Roto-reflection
7. Glide (translation + reflection)
8. Screw (rotation + translation)

Symmetry of Crystal Systems

Crystal System	Axial Relationships	Interaxial Angles	**Minimum # of Symmetry** Elements
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	Four 3-fold rotation or roto-inversion axes parallel to body diagonals
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°; \gamma = 120°$	One 6-fold rotation or rotoinversion axis parallel to z-axis
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	One 4-fold rotation or roto-inversion axis parallel to z-axis
Rhombohedral (Trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	One 3-fold rotation or roto-inversion axis parallel to z-axis
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Three 2-fold rotation or roto-inversion axes parallel to x,y,z-axes
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90° \neq \beta$	One 2-fold rotation or roto-inversion axis parallel to y-axis
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	None

Increasing symmetry

I'd memorize these if I were you

Crystal System

+

Symmetric Array
of Lattice Points

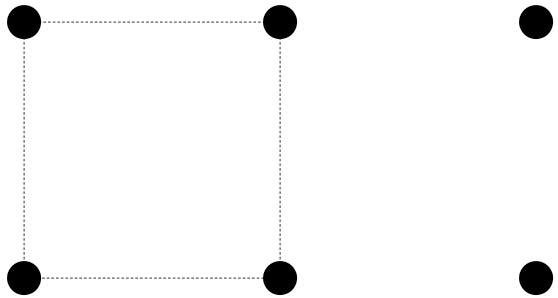
=

Bravais Lattice

We can classify Bravais lattices in terms of the number of lattice points in the unit cell

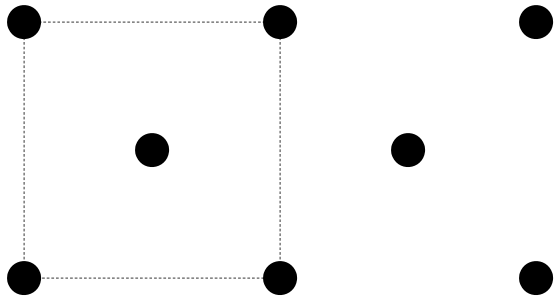
Types of Lattices

- Primitive (P)
  - One lattice point per unit cell
  - Termed “simple” or “primitive”



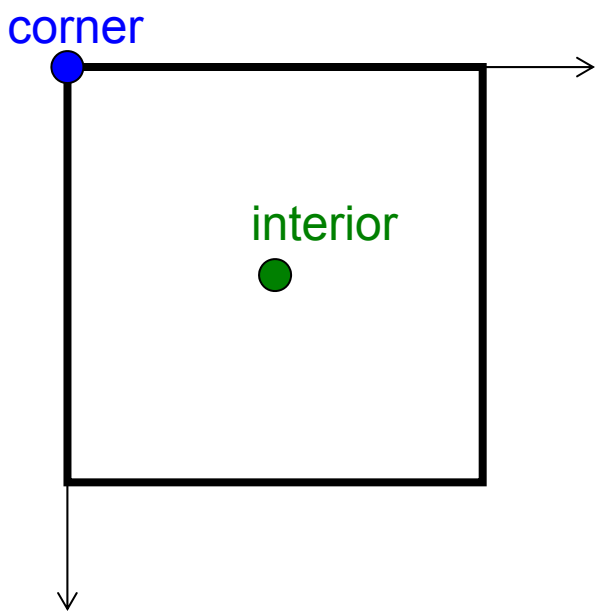
- Non-primitive (multiple)
  - More than one lattice point per unit cell.
  - Termed “XXX-centered”

XXX = body, face, or base



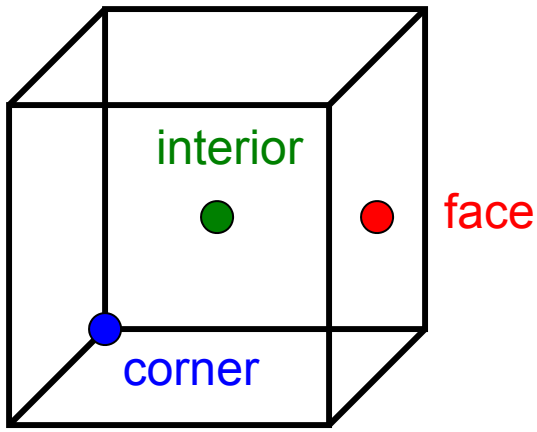
Lattice Points Per Cell in 2D

$$N_{2D} = N_{interior} + \frac{N_{corner}}{4}$$



Lattice Points Per Cell in 3D

$$N_{3D} = N_{interior} + \frac{N_{face}}{2} + \frac{N_{corner}}{8}$$



Primitive vs. Non-primitive lattices

- There are 4 crystal systems in 2D. Thus we can define 4 primitive lattices in 2D.
  - 4 primitive Bravais 'nets' (aka. "lattices")
  - Are there more?

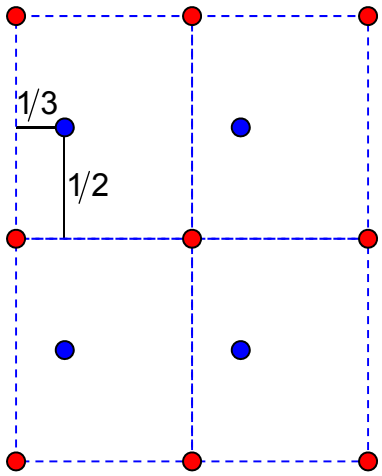
- There are 7 crystal systems in 3D. Thus we can define 7 primitive lattices in 3D.
  - 7 primitive Bravais lattices
  - Are there more?

- Can we add additional lattice points to a primitive lattice and still have a lattice with the same shape?

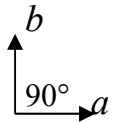
Primitive vs. Non-primitive lattices

- Answer: YES, if we maintain symmetry.

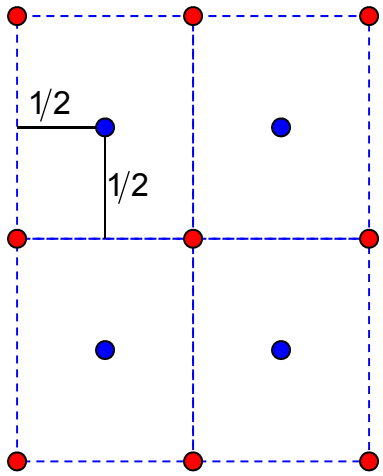
  ("All lattice points must be equivalent.)



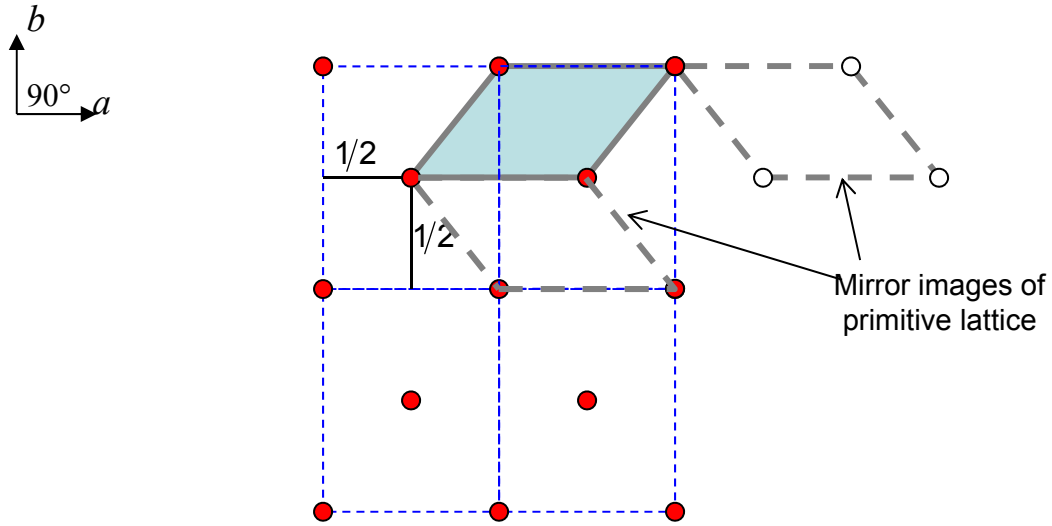
IMPOSSIBLE



2D rectangular lattices



POSSIBLE

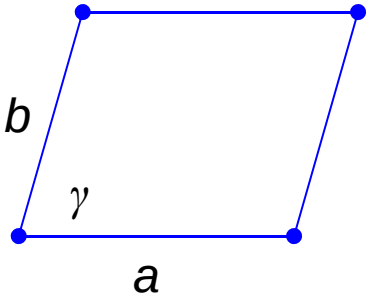


- What if we define a primitive oblique lattice (shaded) rather than a centered rectangle?

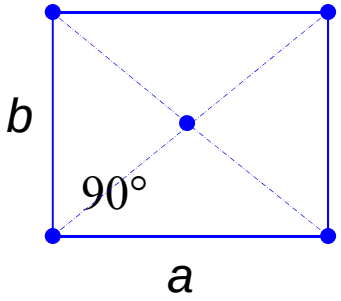
- The primitive cell is less symmetric than the centered rectangle. For example, a mirror image of the primitive unit cell *is not identical* to the original.

  A mirror image of the rectangular cell with a lattice point in the center IS identical to the original. *"It has higher symmetry!"*

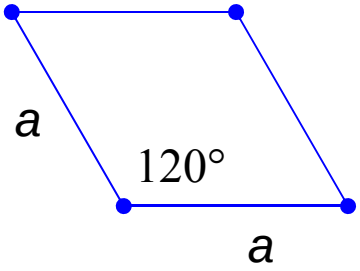
Five 2D Bravais Lattices



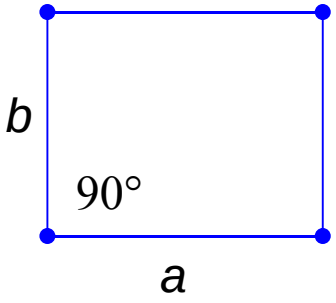
Primitive
Oblique



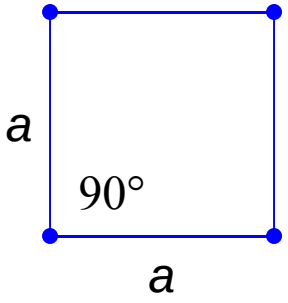
Centered
Rectangle



Primitive
Hexagonal

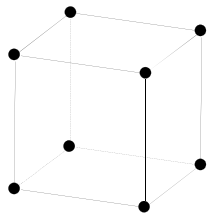


Primitive
Rectangle

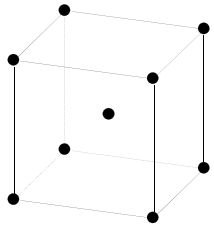


Primitive
Square

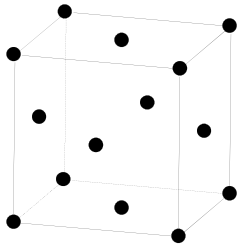
14 Bravais Lattices (three dimensional)



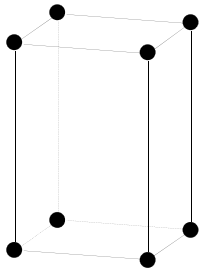
Simple cubic
Cubic P
(1)



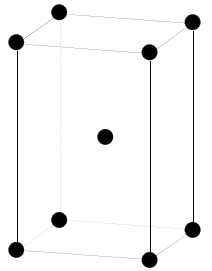
BCC
Cubic I
(2)



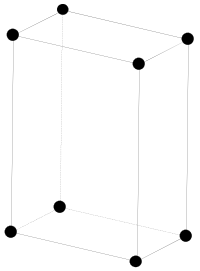
FCC
Cubic F
(4)



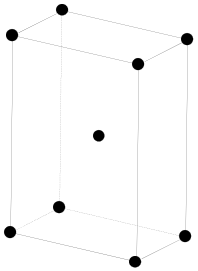
Simple tetragonal
Tetragonal P
(1)



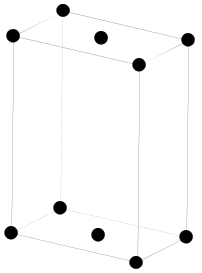
Body-centered tetragonal
Tetragonal I
(2)



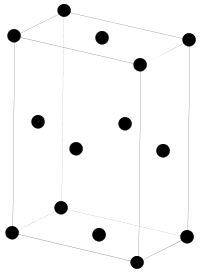
Simple orthorhombic
Orthorhombic P
(1)



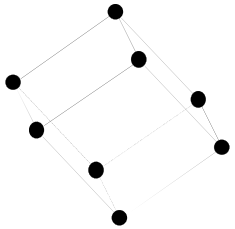
Body-centered orth.
Orthorhombic I
(2)



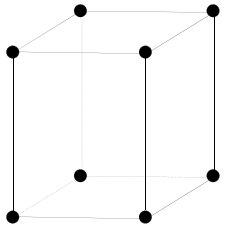
Base-centered orth.
Orthorhombic C
(2)



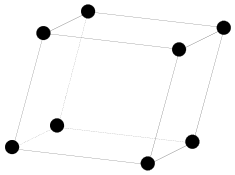
Face-centered orth.
Orthorhombic F
(4)



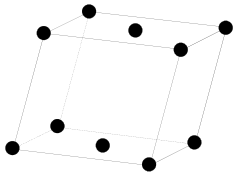
Rhombohedral
Trigonal R
(1)



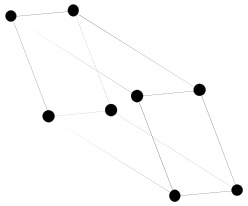
Simple Hexagonal
Hexagonal P
(1)



Simple monoclinic
Monoclinic P
(1)



Base-centered monoclinic
Monoclinic C
(2)



Simple Triclinic
Triclinic P
(1)

primitive

General things about lattices

- RECALL: You can always define a primitive lattice/unit cell.

►HOWEVER, If a non-primitive cell can be found that also describes symmetry of the lattice, it should be used instead.

- Since all lattice points must be identical, new lattice points can only be placed on positions "centered" between primitive lattice points.

Don't confuse lattice points with atoms

- Now you know how to define a crystal in terms of symmetry operations.

- Next we shall address relationships between crystal planes and directions.
  - Miller indices
  - Stereographic projections
  - Reciprocal space