L2: Crystal lattice and unit cell

Wednesday, July 22, 2020 18:02

Time on task: about 2 hours (Material posted on Aug. 24th, Office hours: Wednesdays, Sept 2nd and Sept 9th)

Goals:

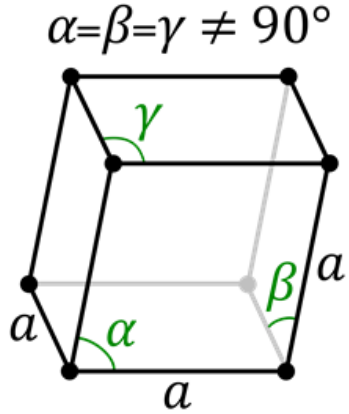
Upon completion of this lecture, you should be able to:

1. Fully describe the seven crystal systems
2. Find the unit cell and describe the lattice in 2D and 3D structures

This lecture is complemented with your Problem set #1 (due on Friday Sept 18th)

Dolomite

Ankerite



Trigonal crystal system

Now that we have introduce the macroscopic properties, for the next month or so, we will discuss the atomic structure of the crystals and we will try to understand how to relate atomic **structure** to macroscopic properties.

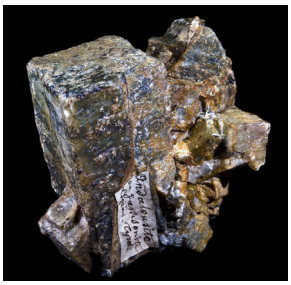
1. Introduction: Structure vs. composition

Some minerals share a similar structure but have different compositions.

e.g., Dolomite ($CaMg(CO_3)_2$) and Ankerite $Ca(Mg,Fe,Mn)(CO_3)_2$: both are carbonates, but dolomite has a fix composition while Ankerite can present in a range of compositions because Mg^{2+} can be substituted with Fe^{2+} and/or Mn^{2+}. We says that ankerite is a **solid-solution** and that dolomite is the magnesium **end-member** (or Mg pole) of this solid-solution. However, the crystal structure stays the same: **trigonal**.
Note that most of the macroscopic diagnostic property between the two minerals are very similar: tabular habit, hardness 3.5-4, vitreous luster, white streak, brittle, rhombohedral cleavages. The color, however, is usually not the same.

Other minerals share the same composition but have different crystal structures. We call them polymorphs.

e.g., Andalusite and Kyanite (composition: Al_2SiO_5)



	Andalusite	**Kyanite**
Crystal system:	orthorhombic	triclinic
Habit:	prismatic/columnar	Bladed
Color:	mostly brown	Blue
Hardness	6.5-7.5	4.5-5 or 6.5-7 (change with the orientation)
Streak:	white	white
Specific gravity	3.17	3.67
Cleavages	2 good, one poor	2 perfect, one good

This time, most diagnostic properties differ between the two minerals!

Overall, **the atomic structure controls the macroscopic (and many microscopic) properties of the minerals,** not the composition. Composition mostly affects the color and can also affect the density. (but we just saw that the atomic structure also affect those properties).

Can you think about another famous pair of polymorphs that show very different macroscopic properties?

L2: Crystal lattice

Wednesday, July 22, 2020 18:57

2. Crystal lattice 101

"**A crystal** is a homogeneous chemical compound with a regular and periodic arrangement of atoms. These arrangements present symmetries." (see L1.1)

In other words, a crystal consists of atoms, molecules or ions in a **pattern** (=arrangement) that **repeats** (= are periodic) in three dimensions.

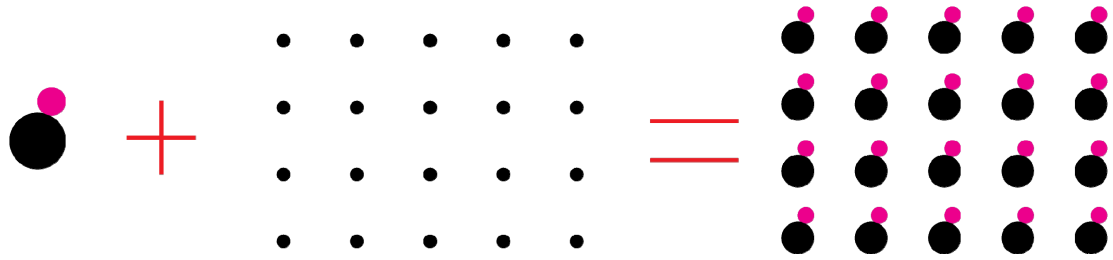
Lattice points are points that are **identical** throughout the crystal. You should be able to move from one lattice point to another through **translation** and keep the exact same environment. The choice of the lattice point is arbitrary. It can be the points of higher symmetry in the motif. We also often choose the point of higher symmetry.

The **crystal Lattice** is constructed by connecting lattice points through the crystal.
Keep in mind that we usually only represent a small amount of lattice points. Lattice can extend in all directions.

Terminology used in PS1 and PS2:
Motif/base = drawing/shape/atom/group of molecules present at a lattice point. By moving from one lattice point to another, you will reproduce the exact same drawing/shape/atom/group of molecules in the **exact same orientation**. We usually choose the smallest motif as possible.
Lattice: array described by the lattice points
Pattern = Motif + lattice. Would correspond to the crystal structure.
Examples:

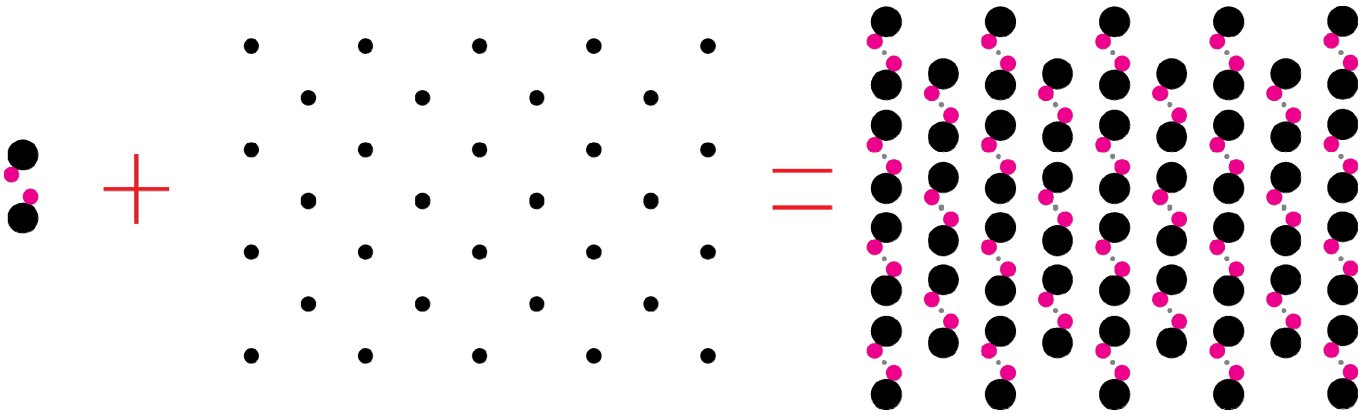
- In 2D:

Example#1



Motif/base **Lattice** **Crystal/pattern**

Example#2



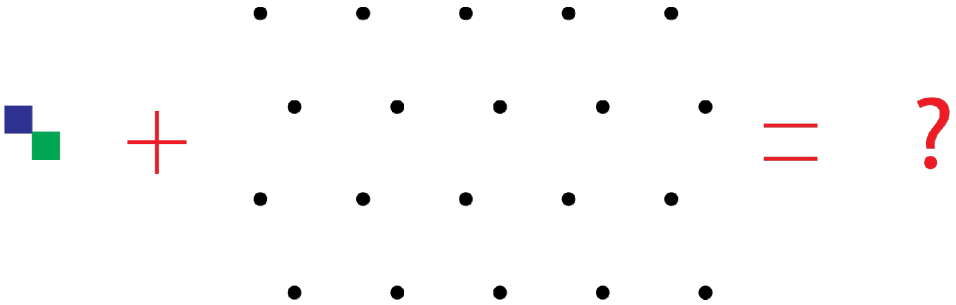
Motif/base **Lattice** **Crystal/pattern**

(1) We usually don't represent the lattice (or lattice point) in the crystal structure. In this 2nd example, I represented the lattice in the crystal structure with the small grey dots to help you visualize the relationship between the motif, the lattice and the crystal structure.

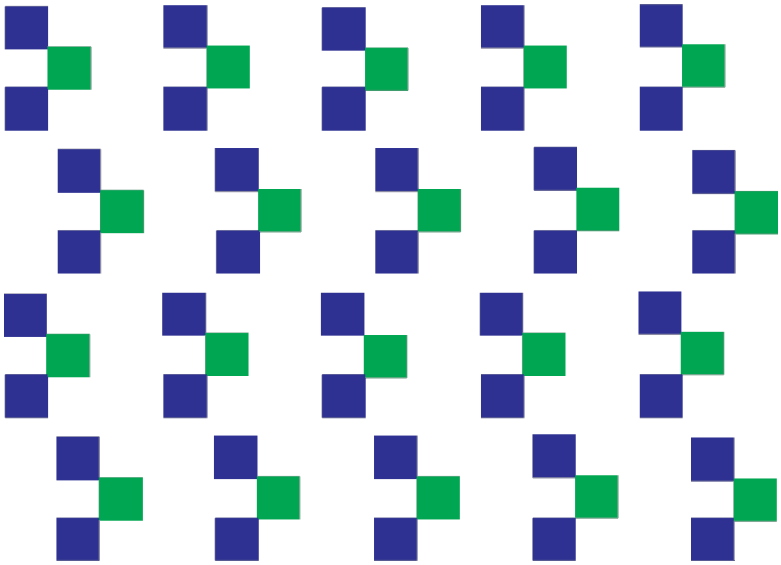
(2) I choose to place my lattice point just in the middle of the motif because that corresponds to the point of higher symmetry.

Your turn! (keys for these small exercises are at the end of this section.)

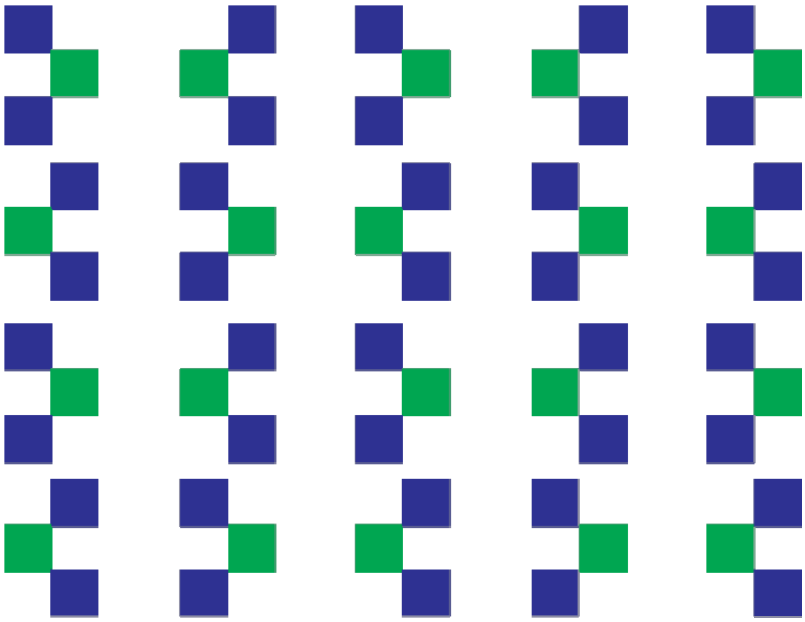
1) Grab a sheet of paper and draw the corresponding crystal structure to the motif and lattice represented below.



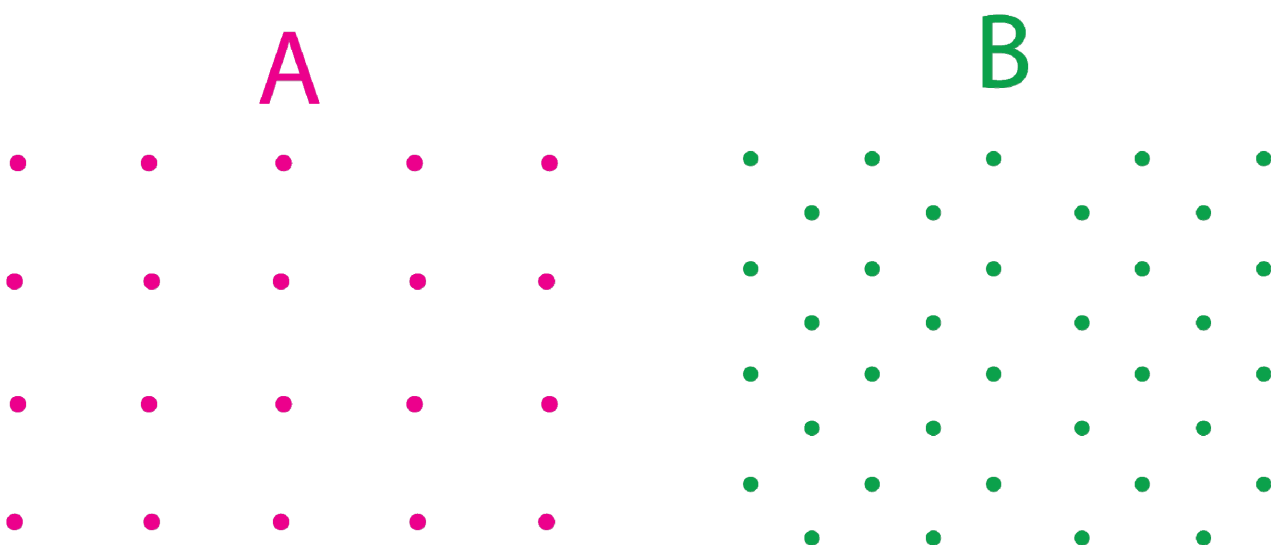
2) Find the smallest motif in the crystal structure below:



3) Find the smallest motif in the crystal structure below:

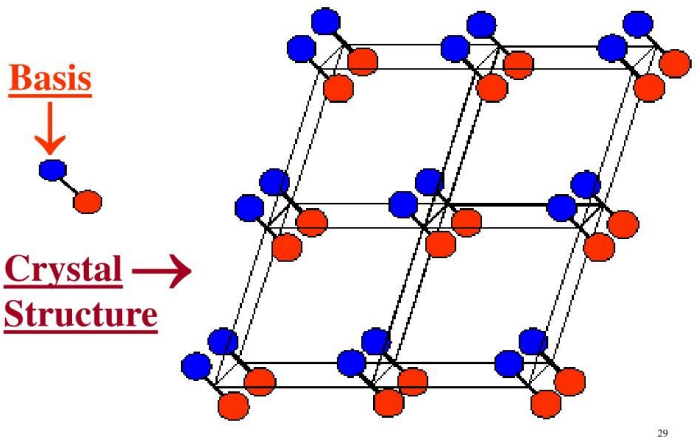


4) A bit more difficult: What is the correct lattice for the crystal structure above, A or B?



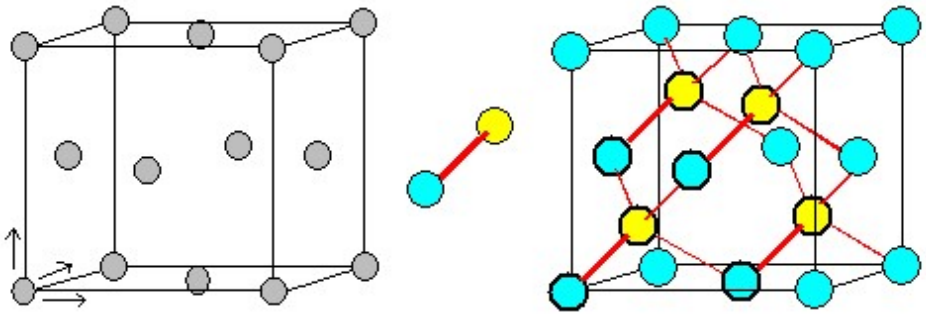
- In 3D:

Example#1



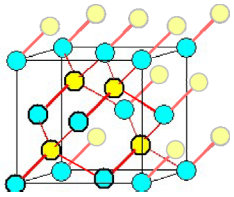
Note: In 3D, the lattice is represented by parallelepipeds. 4 parallelepipeds are illustrated on this figure. At each corner of the parallelepipeds lie a lattice point (not represented here).

Example#2



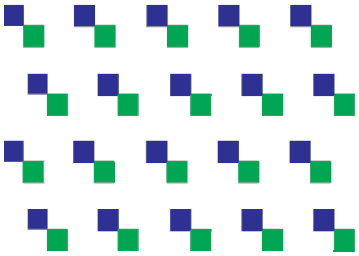
Lattice + Motif = Crystal

We often only represent one parallelepiped (= unit cell) and only the complete motifs that fit inside of the parallelepiped .
In this second example, you have to imagine that each blue atoms is linked to a yellow atom but only the yellow atoms that fall inside the parallelepiped are represented

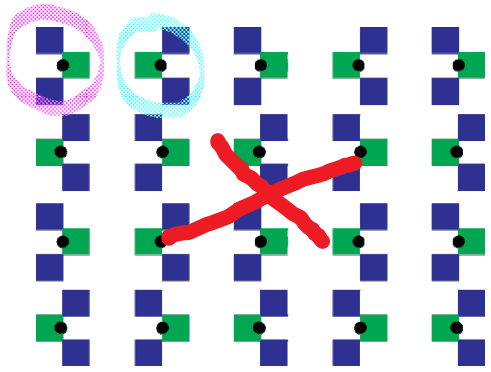


Keys of the practice examples above:

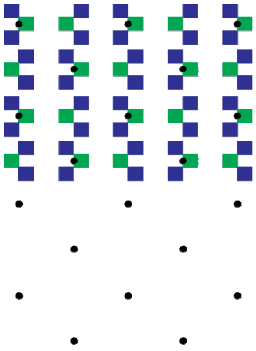
1)



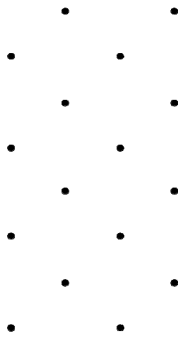
2)



3)



4) B



In A, the two circles black dots can't be two lattice point. The environment of both dots are not identical (there is a mirror symmetry between those two dots.
The correct answer is B. The only diffence between 3) and 4)B is the number of lattice points that are represented. There is 4 times more lattice points represented in 4)B. But remember, you always have to consider that those representation can be expanded to infinity in both directions, vertical and horizontal.

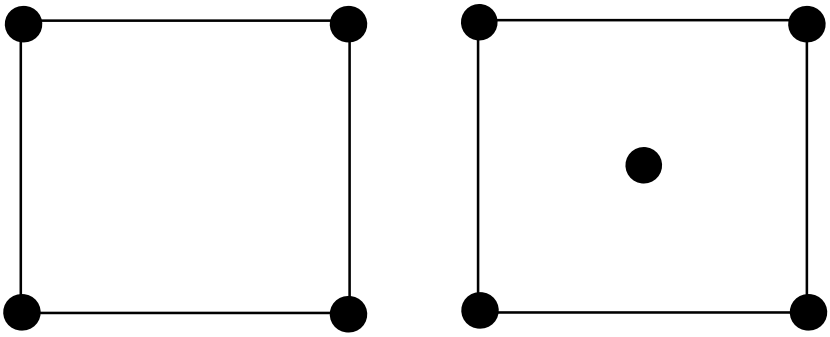
L2: Unit cell and 2D crystal lattice

Thursday, July 23, 2020 12:54

2.1. Unit Cell

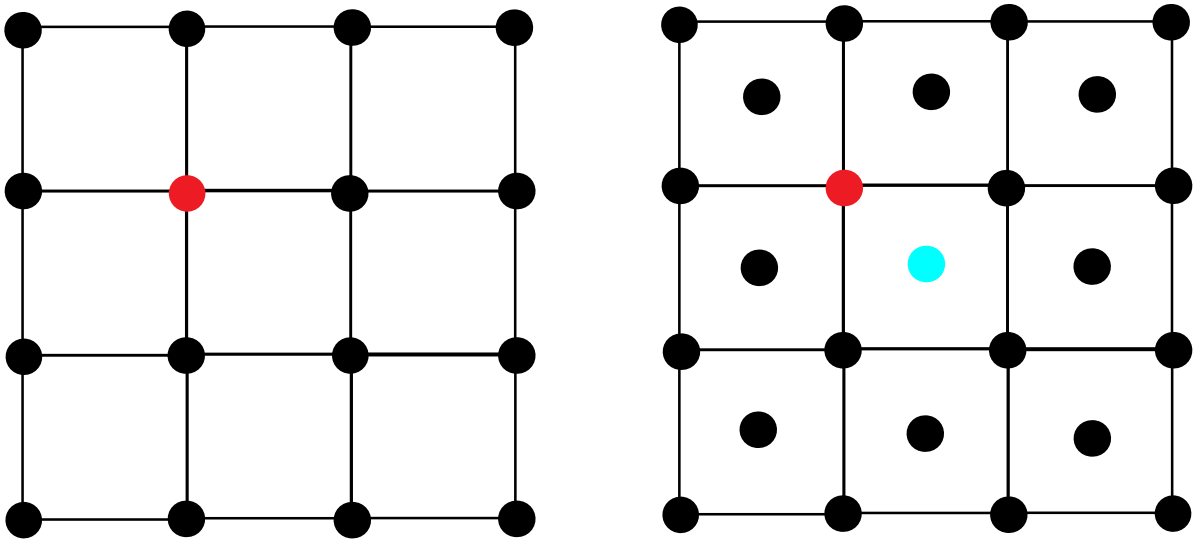
The unit cell is the basic parallelogram constructed by connecting four lattice points (in 2D) or the basic parallelepiped constructed by connecting eight lattice points (in 3D) .

- **In 2D**, we distinguish between primitive and centered unit cells:



Primitive **Centered**

The primitive unit cell has lattice point only at the corner of the parallelogram.
The centered lattice cell has lattice points at the corner and an additional lattice point in the middle of the unit cell.
The crystal lattice is define by the translation of the unit cell in both directions (vertical and horizontal)



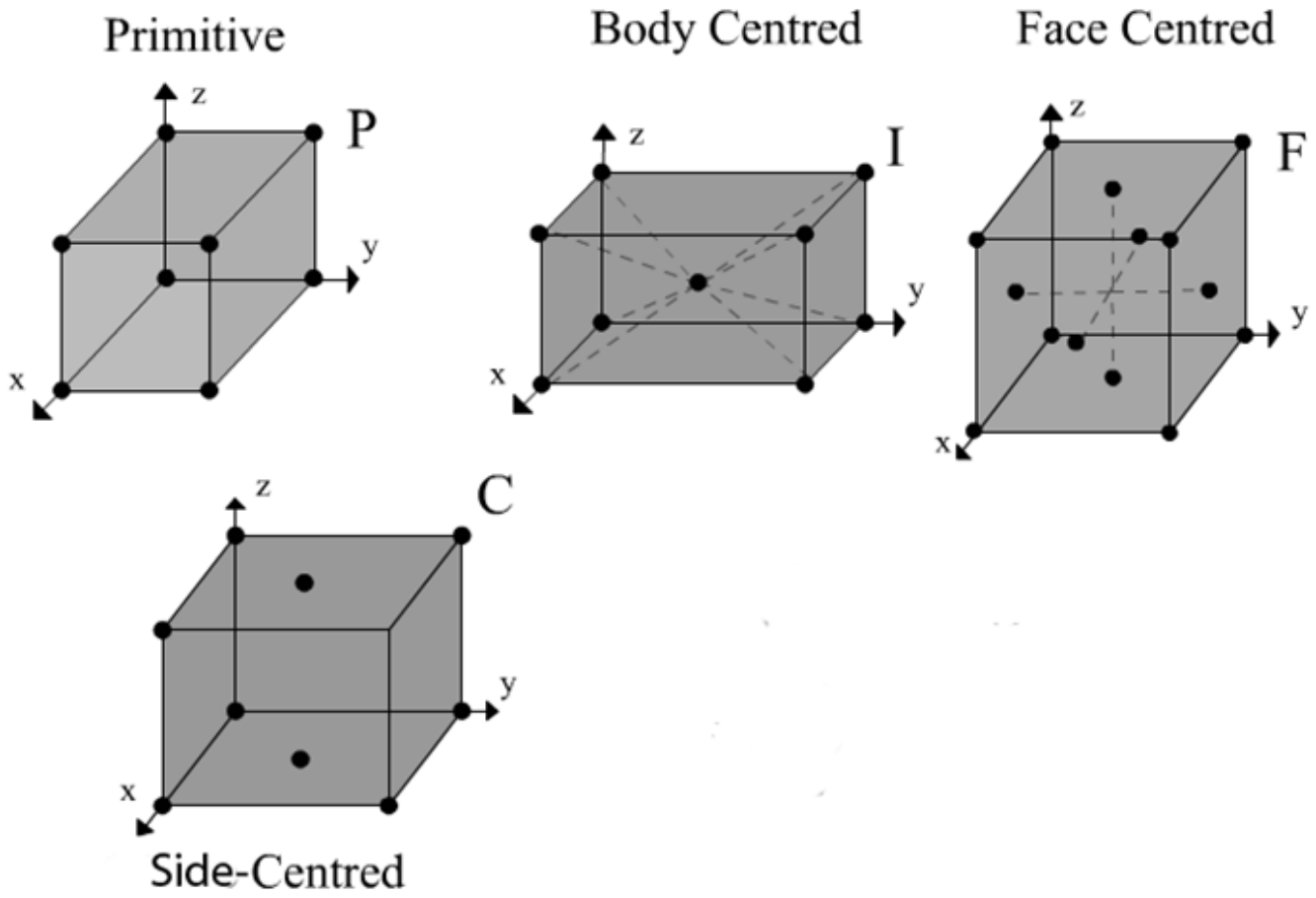
As you can see, each lattice point at the corner of the unit cell is shared between four unit cells. In other words, a unit cell has 1/4 of lattice point at each corner. On the contrary, the lattice point in the center of the centered unit cell is not shared with other unit cell.

Hence: a primitive cell contains 4*1/4 = 1 lattice point
a centered lattice point contains 4*1/4 + 1 = 2 lattice points.

- **In 3D,** we have four types of unit cell.

(P) Primitive
(I) Body Centered (one lattice point in the middle of the parallelepiped)
(F) Face centered (no lattice point in the middle of the parallelepiped but one lattice point in the middle of each face)
(C) Side-centered (only one pair of faces, on opposite sides, has a lattice point in the middle)

Using the same logics than above, try to figure how many lattice points are on each type of unit cell (the answer is below).

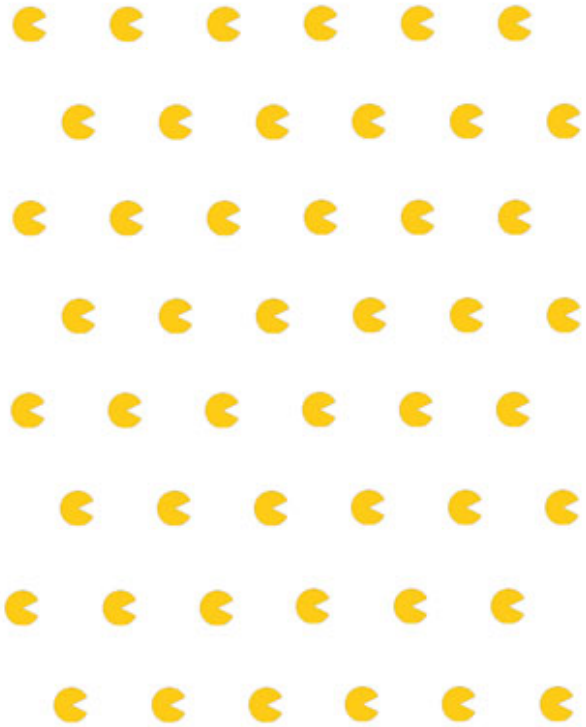


a primitive cell (P) contains 8*1/8 = 1 lattice point
a body centered cell (I) contains 8*1/8 + 1 = 2 lattice points.
A face centered cell (F) contains 8*1/8 + 6*1/2 = 4 lattice points.
A side centered cell (C) contains 8*1/8 + 2*1/2 = 2 lattice points.

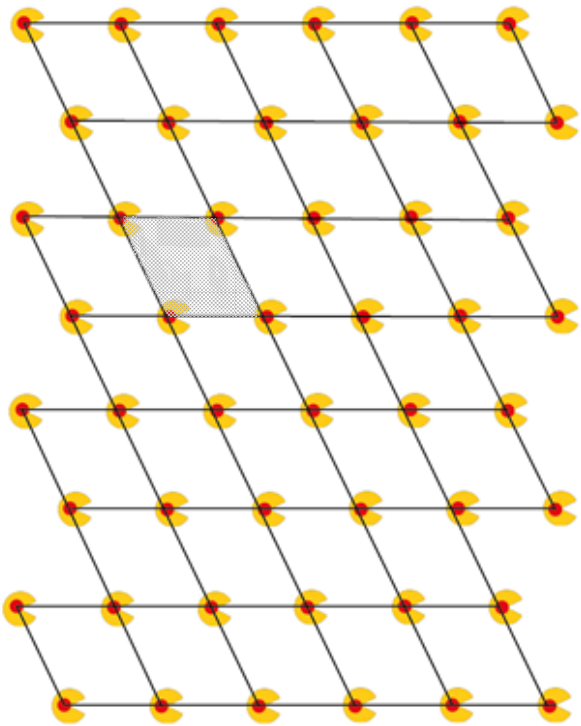
2.2. Choice of the unit cell/crystal lattice

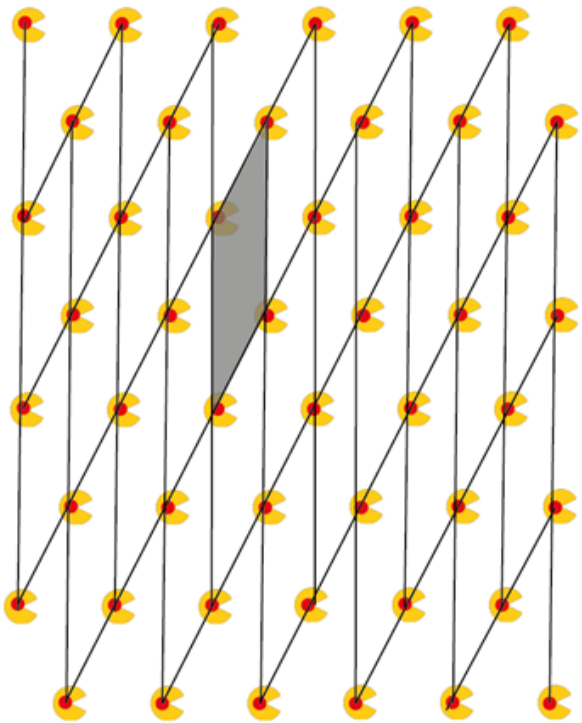
As mentioned in the previous section, a crystal lattice is built by connecting adjacent lattice points into parallelograms/parallelepipeds and each of these parallelogram/parallelepiped represent a unit cell.

As an example, let's consider the 2D crystal structure bellow.



The motif/base is the Pacman shape. Now that you have identify the motif and the lattice points (e.g., the middle of the Pacman), you can draw the lattice. Problem: they are several way to connect those lattice points together and the unit cell won't look the same depending on the choice you make.
e.g.,



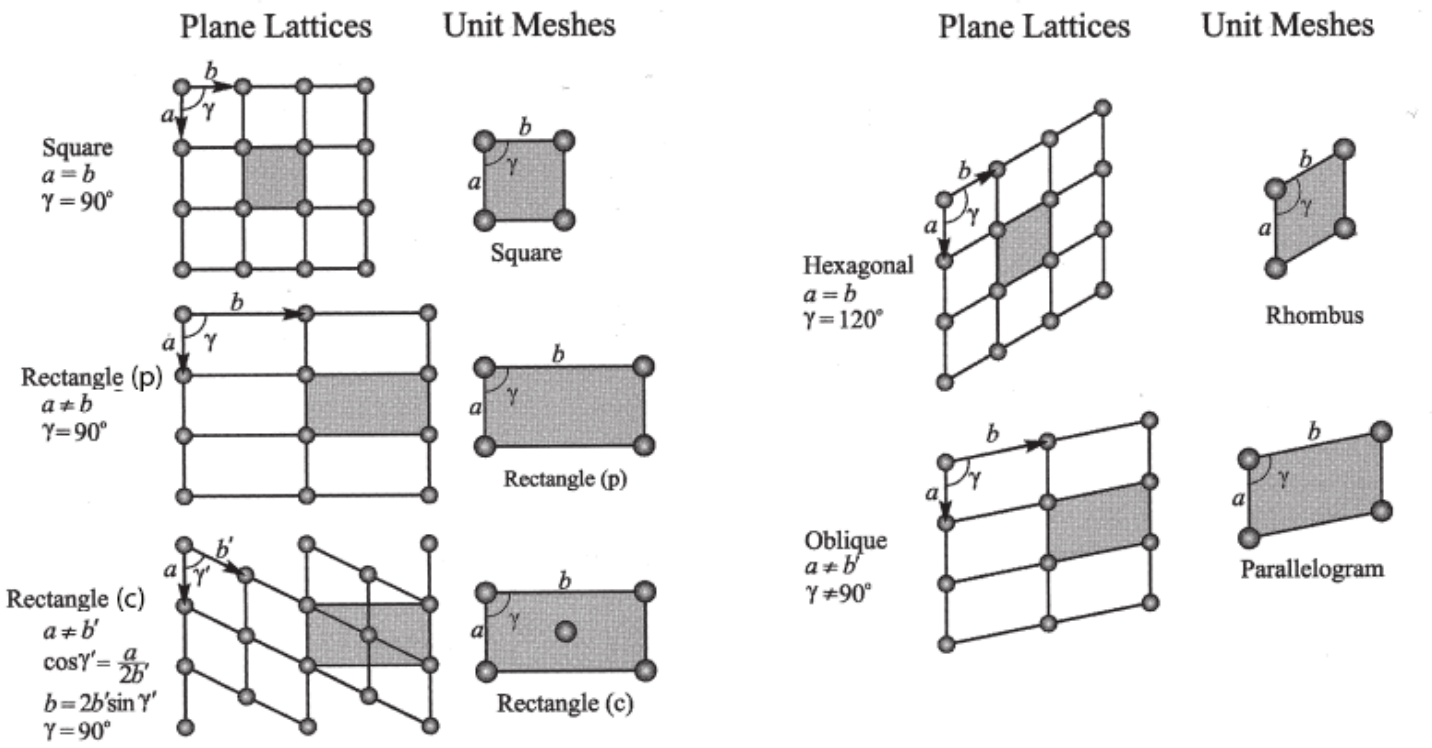


With more than 5700 minerals on Earth (and many more synthetic crystals), mineralogists need to make sure they all describe the unit cell (including dimension and angles) the same way!

They are two rules:
(1) the unit cell is always a parallelogram in 2D and a parallelepiped in 3D.
(2) the chosen unit cell must have the highest possible symmetry and must be the smallest as possible (both parameters are equally important)
If, for one array of lattice point, you can built several different crystal lattice, you choice should always follow these two rules.

In 2D, we have 5 types of crystal lattice possible depending of the choice of unit cell:

- **Square:** 90° angles and same distances between each latticce point in both directions
- **Hexagonal or rhombus:** the unit cell displays a 120° angle between the two sides, but keep the same distances between each lattice point in both directions.
- **Primitive rectangle:** 90° angles but different distances with each lattice point between both directions
- **Centered rectangle:** 90° angles but different distances with each lattice point between both directions and a lattice point in the middle of the unit cell.
- **Oblique:** angle ≠ 90° and distance and different distances with each lattice point between both directions and a lattice point.

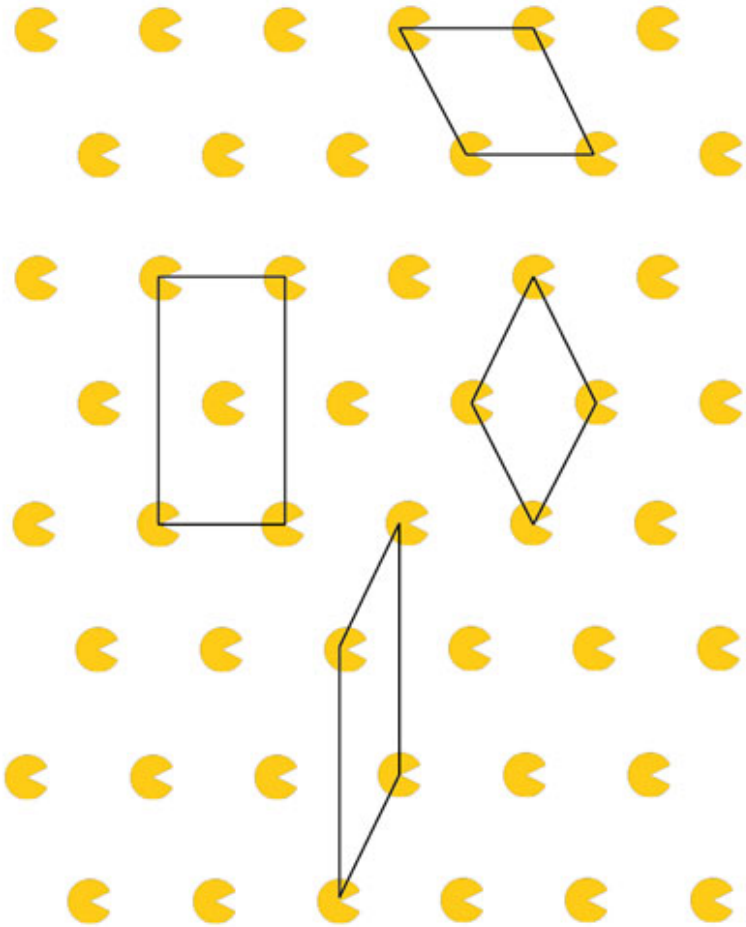


Modified from Fig. 2.2 in Nesse (Introduction to Mineralogy - 2nd edition)

The degree of symmetry for these 5 crystal lattices is: square>rhombus>primitiverectangle>centered rectangle>Oblique

Please note that in practice, the distinction between Rectangle (c) and hexagonal might be hard to do. The key is in the hexagonal lattice, the sides of the unit cell have the same length.

Back to our "Pacman crystal", we have indeed several possibility for unit cell. Which one do you think we should choose?



L2: Crystal systems and 3D Bravais lattices

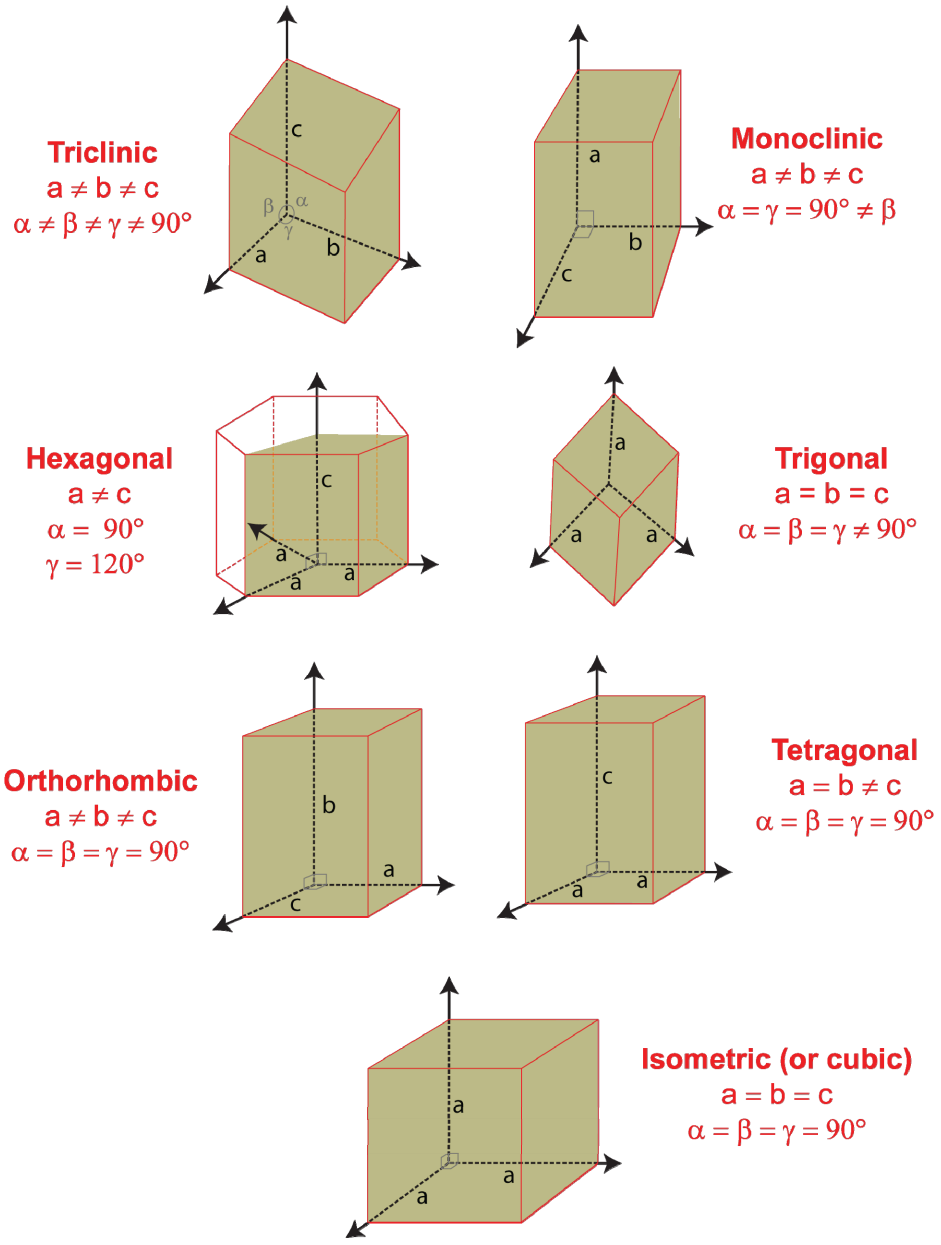
Thursday, July 23, 2020 22:46

3. Crystal lattice in 3D

3.1. The seven crystal systems

The same way that in 2D, we can have various "shapes" of parallelogram describing unit cells (square, rhombus, rectangle and regular parallelogram), we have various "shapes" of parallelepiped in 3D. These various shapes are what we call **the seven crystal systems**. Each crystal system is defined by 3 axis lengths (a, b and c) and the three angles between these three axes (α: angle between axes b and c, β: angle between a and c, γ: angle between a and b; see example on the triclinic system below). The hexagonal system is the only one defined by 4 axes.

You should be able to name and describe (relative dimensions and angles) of each crystal systems. Start practicing now, this will come back often and regularly during the semester!



- Triclinic: no right angles and none of the faces are identical.
- Monoclinic: a pair of faces are rectangles, the 4 other faces are parallelograms
- Hexagonal: a pair of hexagons and 6 identical rectangles
- Trigonal: 6 identical rhombus
- Orthorhombic: 3 pairs of rectangles
- Tetragonal or quadratic: a square base and 4 identical rectangles
- Isometric or cubic: 6 identical square.

To visualize the crystal system in 3D, open the **crystal_systems.html** file posted on Canvas with your internet browser.

The shaded/yellow area on each crystal show the corresponding unit cell. *For all but the hexagonal system, the unit cell has the same shape than the crystal system. Remember, the unit cell is always a parallelepiped. We can fill the hexagonal crystal system using 3 unit cells.*

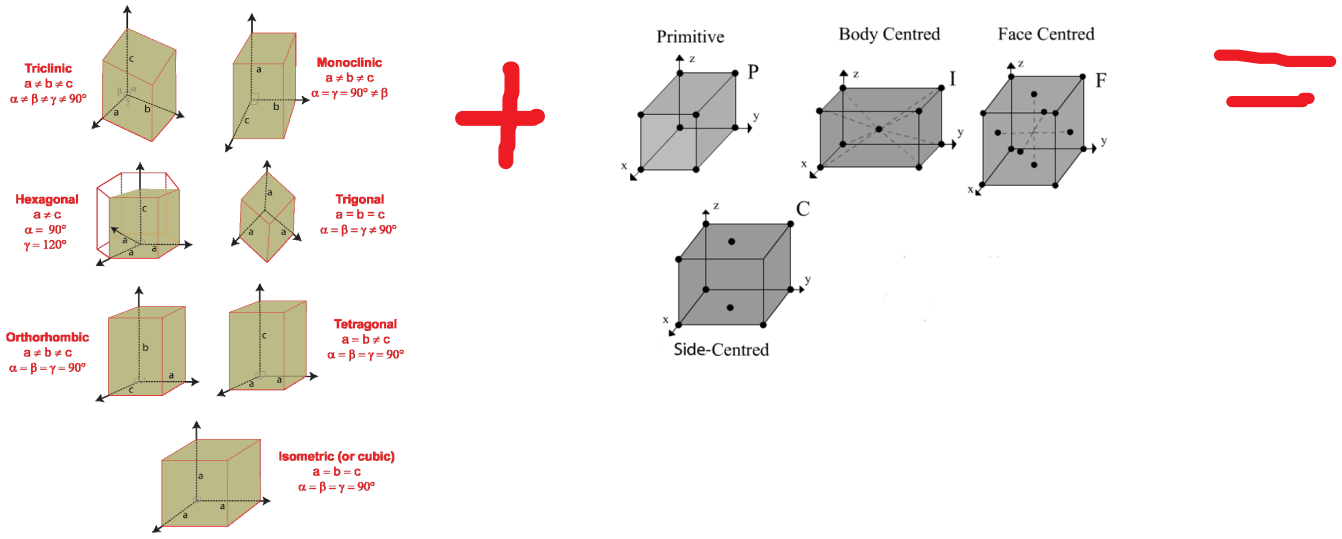
Two important points to remember are that:

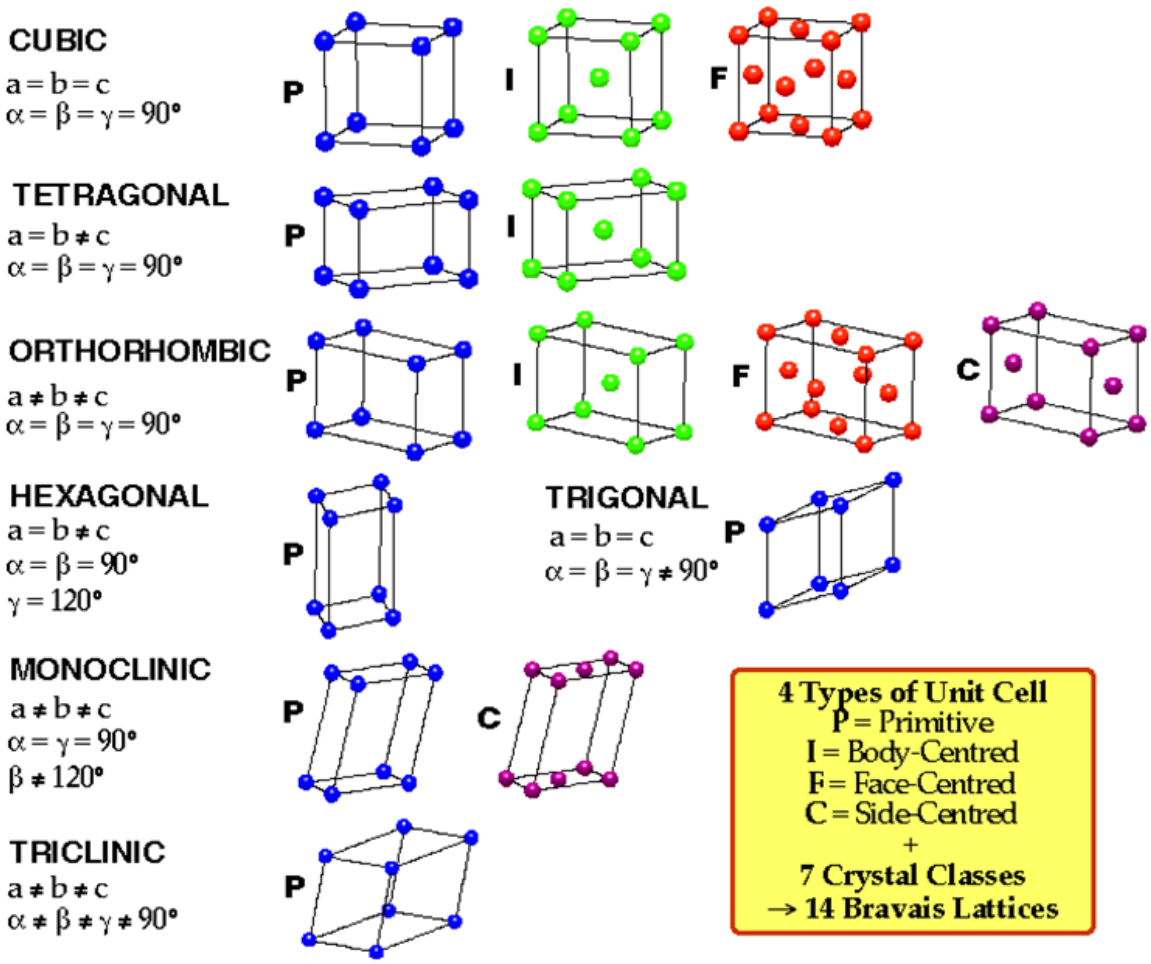
1. **The lengths of the crystallographic axes are controlled by the dimensions of the unit cell.**
2. **The angles between the crystallographic axes are controlled by the shape of the unit cell.**

Convention: When two axes have the same dimension, the third (and unique) one is c.
Note: the trigonal and hexagonal crystal systems are sometime considers as subsystems of the hexagonal system.

3.2. The 14 Bravais lattice.

If we couple the 4 types of 3D unit cell and the 7 crystal systems, we have **14 different types of Bravais lattice** (i.e., 3D crystal lattices).





You don't necessarily need to remember the 14 Bravais lattice, but you do need to understand why these particular types of unit cell are associated with this particular crystal system.

e.g., - The isometric system can have a primitive, a body-centered or a face-centered unit cell. Why can't it have a side-centered unit cell? Because all faces of the unit cell are identical (i.e., squares). Hence we won't be able to identify one particular pair of faces.

- The triclinic system only shows a primitive cell because this system presents no symmetry. Hence, it does not have a center of symmetry where a lattice point would have the same environment in each direction (and would allow to have a body-centered unit cell). And the same logics can be applied to the faces of the crystal system.

This will become clearer as we introduce the symmetry in the next lecture.

L2 - Personal assessment

Monday, July 20, 2020 19:46

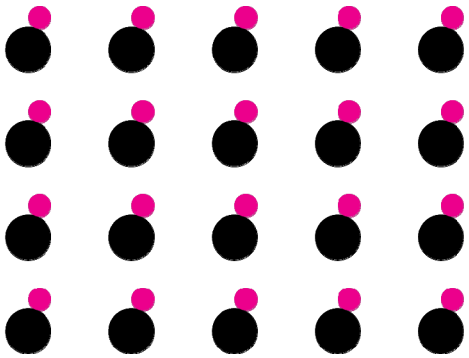
After reviewing the second lecture, you should be able to answer these questions:

****Multiple choices possible!****

1) **The density of a mineral is controlled by:**

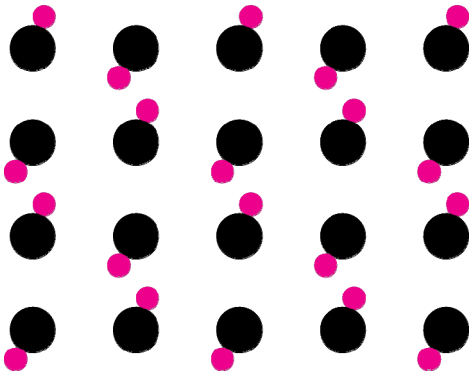
A - The structure of the mineral.
B - The composition of the mineral.

2) **What type of crystal lattice does this 2D crystal describe?**



A - square
B - rhombus
C - rectangle (c)
D - rectangle (p)

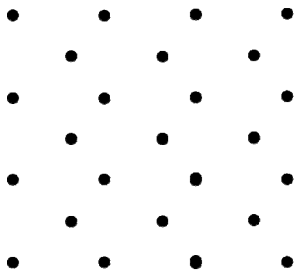
3) **What type of crystal lattice does this 2D crystal describe?**



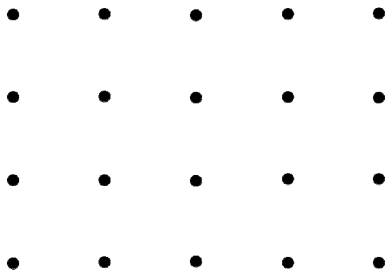
A - square
B - rectangle (c)
C - rectangle (p)
D - oblique

4) **Between these two arrays, which one could be use to describe a crystal lattice?**

A



B



5) **You are studying a subeuhedral crystal that shows a well-developed square face. Based on this information, you can tell that the crystal is:**

A - orthorhombic
B - tetragonal
C - isometric
D - I can't determine the crystal system

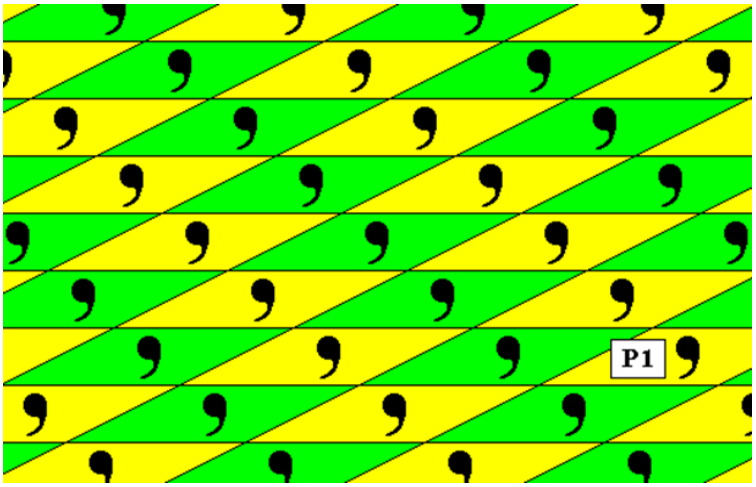
6) **You are studying a subeuhedral crystal that shows two well-developed rectangular faces. Based on this information, you can tell that the crystal:**

A - is not monoclinic
B - is not triclinic
C - is not tetragonal
D - is not isometric

7) **The anion arrangement in this crystal shows a unit cell (F). Based on this information, you can tell.**

A - that its crystal system is isometric
B - its crystal system is not tetragonal
C - its crystal system has at least two equal axis lengths.
D - its crystal system shows only 90° angles

8) **Draw a unit cell on this pattern?** (do not take into account the "P1" square)



9) What is the crystal lattice described by this pattern?

A - oblique
B - rectangle (p)
C - rectangle (c)
D - rhombus

10) Now, assuming that all parallelograms display the same color, draw the unit cell. What is the crystal lattice described by the new pattern?

11) Draw the unit cell corresponding to this pattern