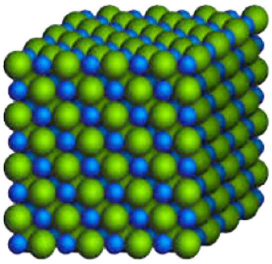
Week 2

A. Crystal systems – we mentioned that crystals are made up of atoms that are arranged in regular, repeating ways in 3-dimensions.

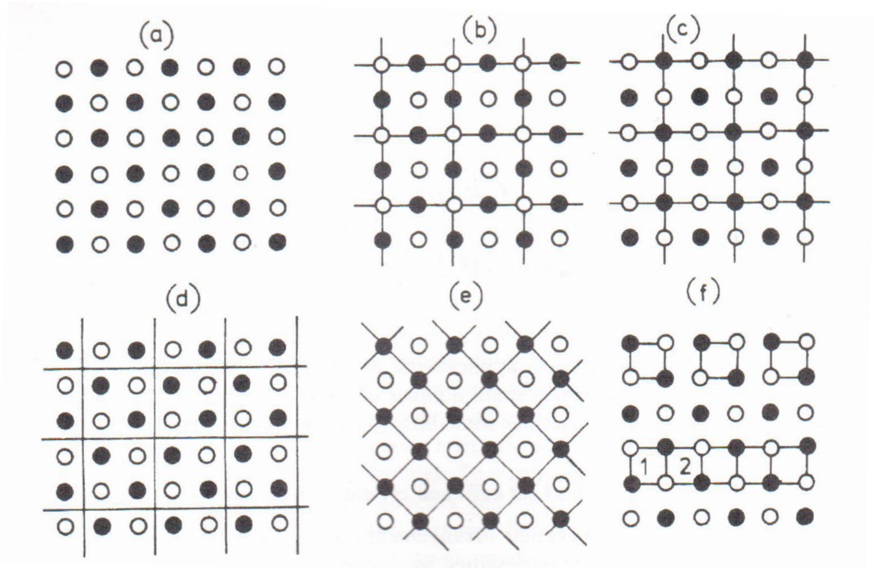
The smallest repeating unit of a crystal is known as the unit cell
The unit cell must possess certain criteria.

1). Smallest repeating unit that reflects all of the symmetry
2). All adjacent unit cells must be the same and connected
3). The choice of the origin can vary – although the size and the shape of cell must remain the same.

The atoms in the unit cell served as lattice points- positions or coordinates of atoms. These points make up crystalline lattices, which can have a variety of different shapes and atom arrangements as we will see later.
Based on these criteria which is the correct unit cell?

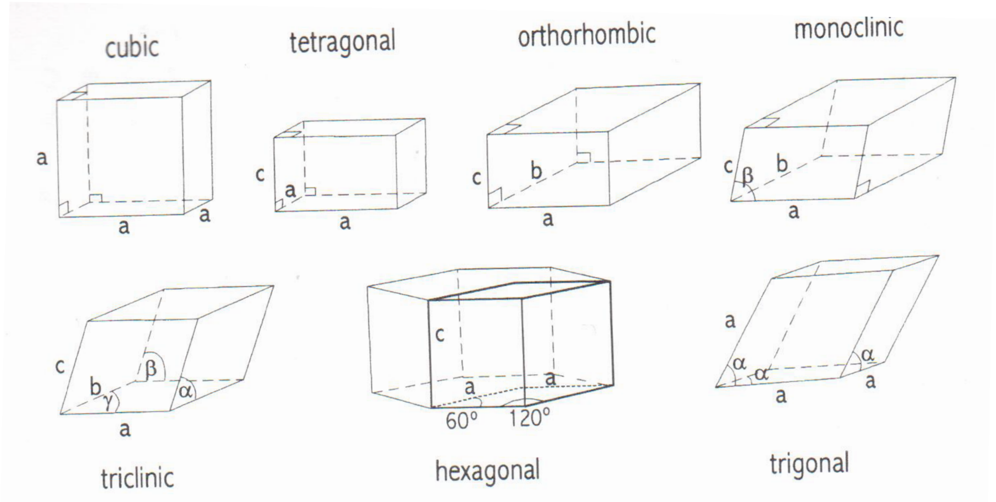


Here I show you a 2-D projection of the NaCl structure. You must pick which unit cell is the proper one based on the criteria I gave you. So, a is just the projection if you take a single row of atoms from the NaCl structure. Then if you look at b, c, and d, they are all the same size. Each unit cell contains two Na and two Cl. All squares chosen are also identical within each picture. Then, you see the unit cell in (e) is smaller, and it still reflects the 4-fold symmetry. There are two atoms per unit cell in this case. In (f) there are two potential unit cel ls shown. In the top part the cells are isolated, and this is not permitted. Further neither reflects the 4-fold symmetry. Last, the bottom part while identical, the orientations are not the same. Na is in the top right of 1 while Cl is in the top right corner of 2.



While (e) is preferred from this 2-dimensional projection. In 3-dimensions (b-d) is the cell of choice because it is the only one that actually shows the cubic symmetry.

There are seven crystal systems that you should know. These represent your unit cells that you can have for a solid material. So, all crystalline solids will be represented by one of these 7. Each crystal systems is determined by the symmetry that is within the unit cell.



So for each crystal system, there are required symmetry elements, before discussing the symmetry elements we should review the symmetry and operations that are used in crystallography and spectroscopy.

Derive this table, start with columns 1 and 2 and add 3 and 4 later.

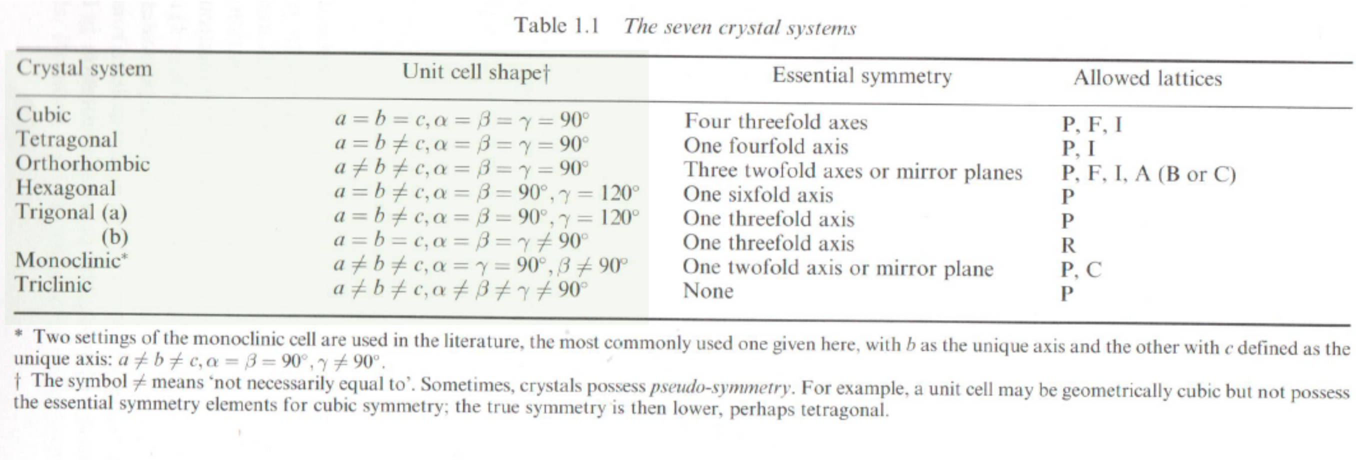


Table 1.1 *The seven crystal systems*

Crystal system	Unit cell shape†	Essential symmetry	Allowed lattices
Cubic	$a = b = c, \alpha = \beta = \gamma = 90^\circ$	Four threefold axes	P, F, I
Tetragonal	$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$	One fourfold axis	P, I
Orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$	Three twofold axes or mirror planes	P, F, I, A (B or C)
Hexagonal	$a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$	One sixfold axis	P
Trigonal (a)	$a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$	One threefold axis	P
(b)	$a = b = c, \alpha = \beta = \gamma \neq 90^\circ$	One threefold axis	R
Monoclinic*	$a \neq b \neq c, \alpha = \gamma = 90^\circ, \beta \neq 90^\circ$	One twofold axis or mirror plane	P, C
Triclinic	$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$	None	P

* Two settings of the monoclinic cell are used in the literature, the most commonly used one given here, with b as the unique axis and the other with c defined as the unique axis: $a \neq b \neq c, \alpha = \beta = 90^\circ, \gamma \neq 90^\circ$.

† The symbol $\neq$ means 'not necessarily equal to'. Sometimes, crystals possess *pseudo-symmetry*. For example, a unit cell may be geometrically cubic but not possess the essential symmetry elements for cubic symmetry; the true symmetry is then lower, perhaps tetragonal.

B. Point Symmetry elements

Point symmetry elements have some point that does not move in space.

Symmetry element	Symmetry operation	Schönflies Symbol (spectroscopy)	Herman-Maugin Symbol (crystallography)
Rotation axis	rotation by 360°/n	C_n	n = 2, 3, 4, 6 5 and 7 Why is this?
mirror plane	Reflection across a plane	σv, σh	m
center of inversion	Inversion -pull atoms through a center point	i	$\bar{1}$
improper axis of rotation aka alternating axis	rotation of 360°/n followed by mirror reflection that is perpendicular to the rotational axis.	S_n	- 2/m 4/m 6/m
inversion axis	Is an n fold rotation followed by an inversion center.	-	$\bar{n} = \bar{3}, \bar{4}, \bar{6}$ etc

Show each element with an octahedron

σ_h indicates a plane which is perpendicular to the highest rotational axis, whereas σ_v is the symbol for **v**ertical mirror planes containing the main axis.

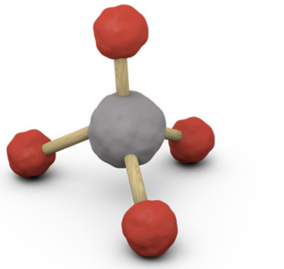
Exercise: Why is there no $\bar{2}$? Work these out using spherical projections.

Answer: A two fold rotation follwed by an inversion is just a mirror plane, m.

Exercise: Why is there no 3/m?

Answer: A 3/m is a $\bar{6}$.

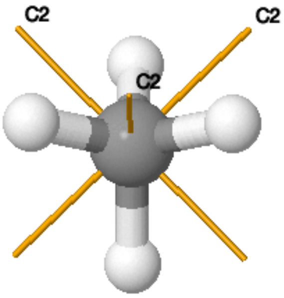
Exercise: Build a tetrahedron. What symmetry elements and how many does SiO_4 how and how many of each?



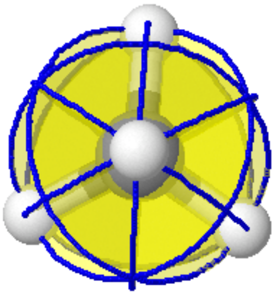
Answer: 4 x 3-fold rotations C_3

3 x 2-fold rotations labeled by green marks – C_2
6 x mirror planes - σd, dihedral mirror plane, which is a σv mirror plane that also bisects C_2 axes.
No inversion center
3 x S_4 (or 4/m) improper axis of rotation and $\bar{4}$ along the C_2 _

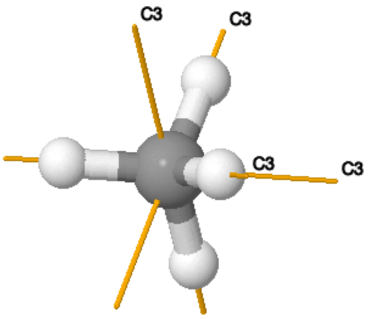
3 x 2-fold rotations



6 x m planes

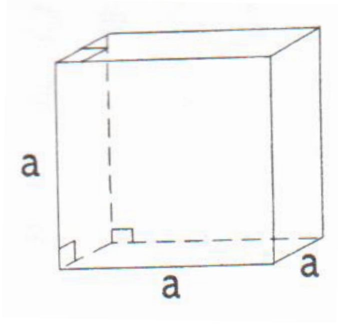


4 x 3-fold rotations



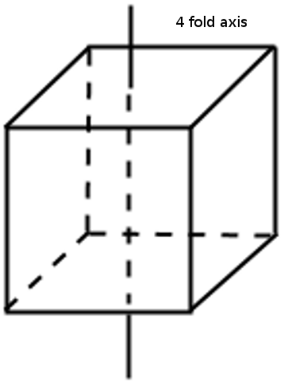
Now that we have reviewed all symmetry, I would like to go back to our seven crystal systems and identify the essential symmetry elements.

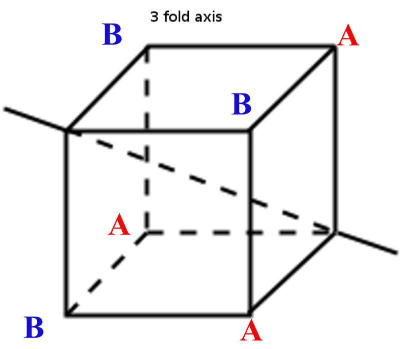
Exercise: Can you identify the rotational axes for a cube?

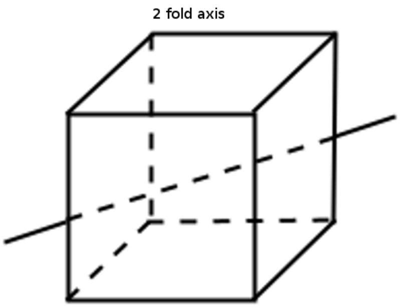


For a cubic unit cell, it is required that it have 4 x 3-fold rotations, which run along the body diagonal. This requires that a, b, and c all be the same and α, β, and γ all be 90°.

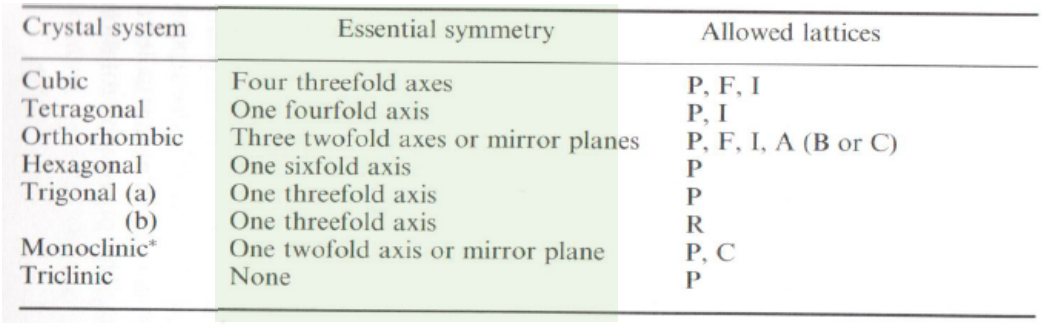
This is the essential symmetry however, a cubic unit cell also has many other symmetry elements by consequence such as 3 x 4-fold rotations, 6 x 2 fold rotations along the cube edge and multiple mirror symmetries.







Essential Symmetry includes:



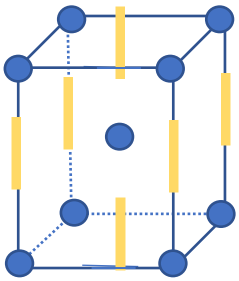
Crystal system	Essential symmetry	Allowed lattices
Cubic	Four threefold axes	P, F, I
Tetragonal	One fourfold axis	P, I
Orthorhombic	Three twofold axes or mirror planes	P, F, I, A (B or C)
Hexagonal	One sixfold axis	P
Trigonal (a)	One threefold axis	P
(b)	One threefold axis	R
Monoclinic*	One twofold axis or mirror plane	P, C
Triclinic	None	P

Tetragonal cell must have a 4-fold rotation axis. It is regarded as a cube that is squashed or elongated. Consequently at 3-fold and 2 of the 4-fold rotations are lost from the original cubic symmetry. So, you will see later when we build different structures that the NaCl structure, which is a cubic unit cell could also be tetragonal, but if this happens the volume is half that of the cubic one; however, you lose certain symmetry elements and so it is instead depicted as cubic.

The tetragonal cell has one unique axis that is different from the others

$a = b \neq c$ and α, β, and $\gamma = 90$.

draw CaC≡C as an example of a tetragonal cell for the class.



You can think of the next cell, the orthorhombic cell as an even more distorted cube where now none of the axes are equal, but α, β, and $\gamma = 90$. The cell must have either 3 two-folds or 3-mirror planes that are perpendicular.

See if I can find a picture with the essential symmetry elements.

Hexagonal unit cell originates from a hexagonal close packing of spheres, which we discuss later. For this cell $a = b \neq c$ and α, $\beta = 90$ and and $\gamma = 120$. Essential symmetry for hexagonal is a 6-fold rotational axis.

In coordination chemistry we discussed a trigonal distortion as being a common one for octahedral geometry. This results from a compression or an elongation along the 3-fold rotational axis of the octahedron. Now the same can happen with a cube. Except here we compress or elongate along the body diagonal of the cube. This results in a trigonal unit cell. This gets diminishes all symmetry associate with the cube other than a single 3-fold axis, which is the essential symmetry associated with a trigonal unit cell. In this case all three edges and angles remain the same, but the angles are no longer = 90.

$a = b = c$ and $\alpha, \beta, \gamma \neq 90$ all angles are the same but not equal to 90. This is referred to as rhombohedral

There are two settings you might see for a trigonal cell and these include the aforementioned rhombohedral or primitive with the following unit cells.

$a = b \neq c$ and $\alpha, \beta = 90$ and and $\gamma = 120$. This is similar to the hexagonal cell but notice rather than a 6-fold rotattion it has a 3 now.

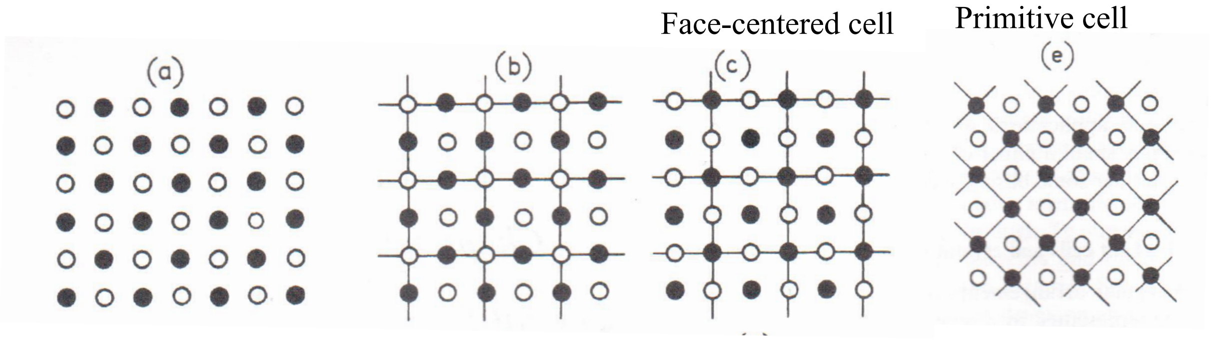
The next is very common and is monoclinic. You can think of this as derived from the orthorhombic unit cell where you shift the top face to the left relative to the bottom. This cause the beta angle to stray from 90 and you lose most of the symmetry apart from a C2 or a mirror plane. In this unit cell the unique axis is defined as b. Because it is from the orthorhombic cell we know $a \neq b \neq c$ and also one angle deviates from 90…. $\alpha, \gamma = 90$ since b is usually defined as the unique axis then angle $\beta \neq 90$. You should note that on some occasions the γ angle is sometimes the one that deviates.

The last system has no essential symmetry. It is called triclinic and $a \neq b \neq c$ *and* $\alpha, \beta, \gamma \neq 90$

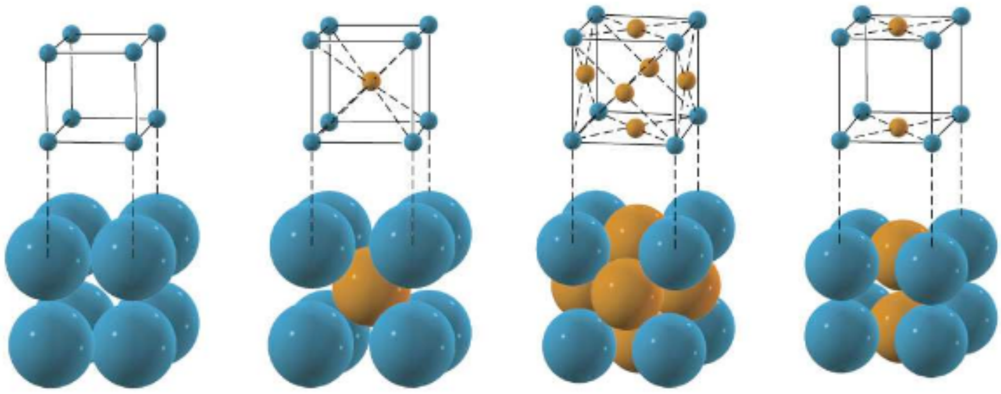
D. 14 Bravais Lattices

Now that we know about the essential symmetry and unit cell shapes we should know about Bravais lattices. Lattice is just a term that describes the array of atoms in a unit cell and the each atom is referred to as a lattice point.

Let's go back to the 2-D projection we had of NaCl



Now lets consider a 3-D cube….



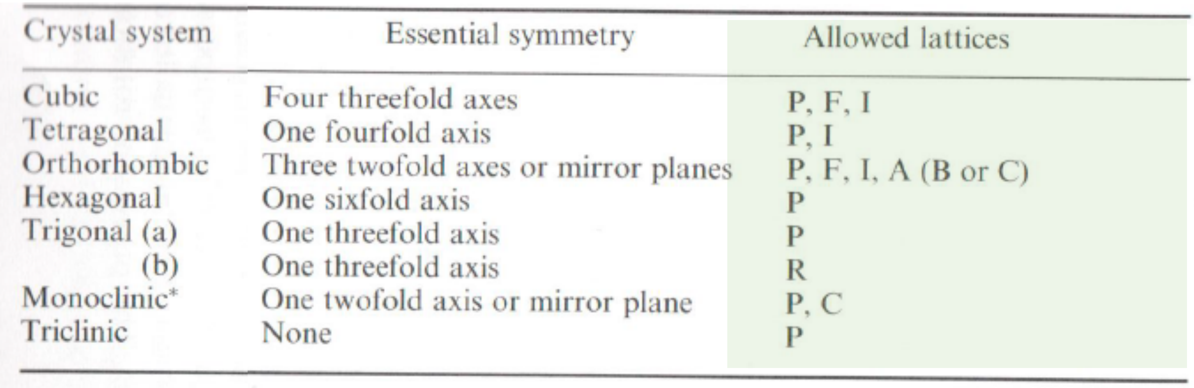
Primitive Body-centered Face-centered Side-centered

Exercise: how many atoms per unit cell?
Answer: 1, 2, 4, 2

So there are symbols. Each of the 7 crystal systems can be P, F, I, or C which describes the crystal lattice type. However, it should be noted that not all of these lattices are allowed for each crystal system.

P means it is primitive
F means it is face centered
I means it is body centered
C (A or B) means it is C-centered. So, you will have an atom in the middle of the face of the structure but not the others.

Now go back to table and put in the potential lattices.



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Monoclinic*	One twofold axis or mirror plane	P, C
Triclinic	None	P

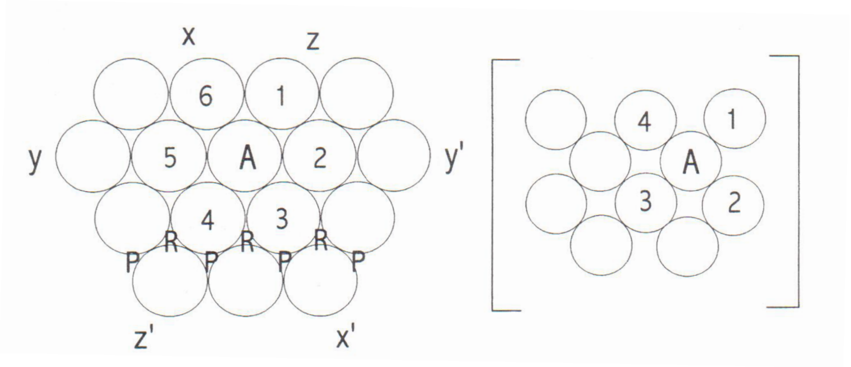
A cubic Lattice can be face-centered, body-centered, or C-centered.

There are 14 possible Bravais lattices. It should be noted that because Rombohedral and Trigonal settings are interchangeable then only the rhombohedral one is included in the most texts as part of Bravais lattices

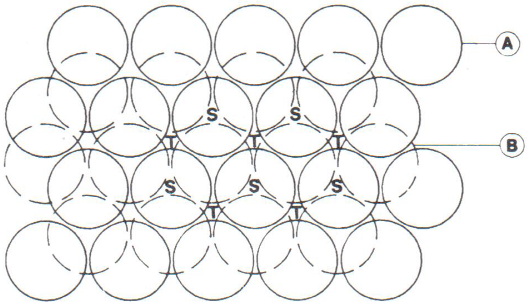
C. Close packed structures

Close Packing Structures: The best way to describe solid structures is through the unit cells which we have discussed before but often times you will see that the materials, particularly ionic ones, and at times covalent and molecular structures, where you have an array of spheres and the structures will be described by close packing. There are two efficient ways to pack spheres in 3-D The two possible ways that the spheres pack is hexagonal close packed and cubic close packed. For both structures, the first layer, A, is surrounded by 6 nearest neighbors. The maximum CN number within the plane is 6. Smaller coordination numbers, such as 4 are also possible. So for both of these structures the second layer of spheres rest in the hollow formed by three spheres in the bottom layer.

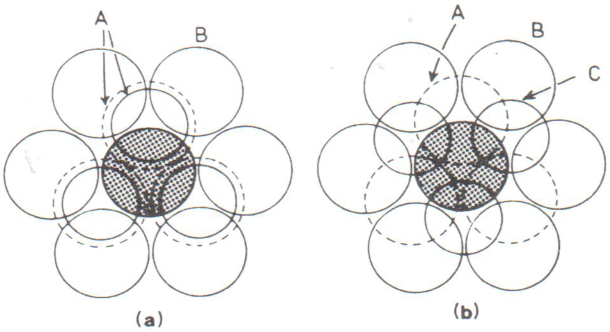
For hcp – layers form an ABABAB type repeat
For ccp – layers form an ABCABC type repeat.



If you have one layer with 6 nearest neighbors then you can see that there are two options for the second layer labeled R and P shown above and then after you add the second layer you can have two options for the 3^{rd} layer. I can be in S which is directly over A, leading to an ABA type packing and hence a hexagonal close packed structure. Or the third layer can go in T and hence be different from layer A and B, see below. This leads to ABC packing and hence is cubic.



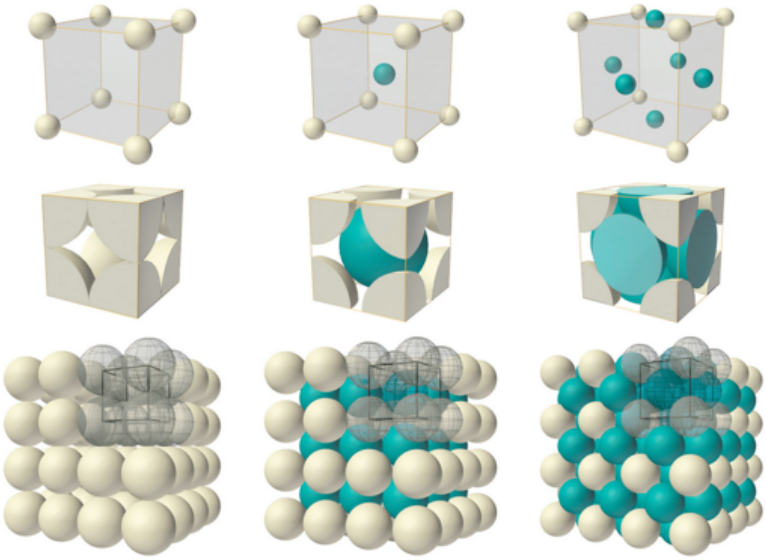
So you can see ccp versus hcp below.



(a) (b)

You should also know that there are of course other more complicated repeat units like ABCACB or ABAC, and these are referred to as polytypism. In a cp structure the coordination number is 12. 6 in the same plane and then 3 above and 3 below.

Exercise: Of these cubic structures, which shows a cp structure type?



P

atoms per cell = 1
CN # = 6

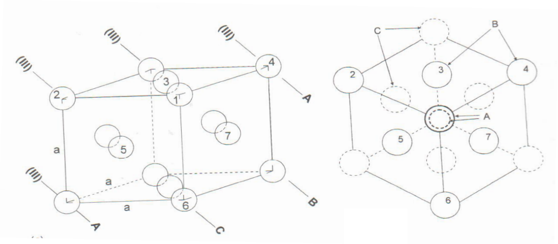
I

atoms per cell = 2
CN # = 8

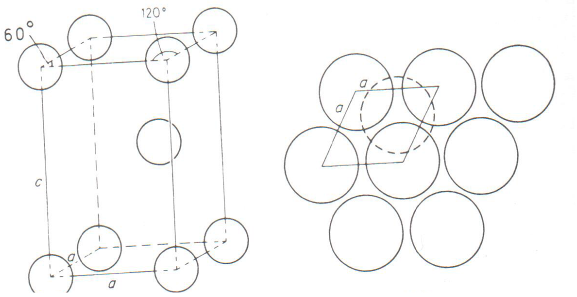
F

atoms per cell = 4
CN # = 12

Answer: F-centered cubic is CCP with ABC type packing. The other two structures are non-close packed. Six nearest neighbors in the same plane as the grey sphere and then 3 above and 3 below for a coordination number of twelve. Below are two different views showing the ABC packing. The one on the right goes along the 111 plane (body diagonal)

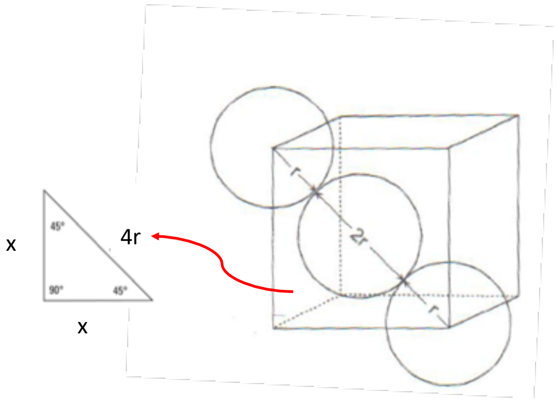


For an HCP array the best way to describe it is with a cell having atoms at the origin (the corner of the cell) and then there is an extra atom with the cartesian coordinates 2/3, 1/3, 1/2 and the c axis is a 3-fold rotation axis.



In CP structures ~74% of the total volume is occupied by the spheres. This is the maximum density possible for structures only constructed by spheres of only a single size. For a non cp structure like bcc the maximum is ~68%.

Exercise: Can you calculate the 74% packing efficiency mentioned above?



0.74 = volume of spheres/volume of cell

1). Lets first determine the volume of the box in terms of r, the radius of the close packed spheres.

Due to the close packed structure the face diagonal in the cell is = 4r.

The Pythagorean theorem says $x^2 + x^2 = z^2$
As such, $2x^2 = 16r^2$
Then $x = 2r\sqrt{2}$
And the cell volume = $16r^3\sqrt{2}$

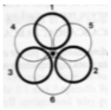
2) Now we must determine the volume of the spheres.
In general the volume of a sphere is $4/3\pi r^3$

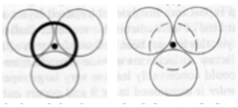
How many spheres are there in a FCC array?

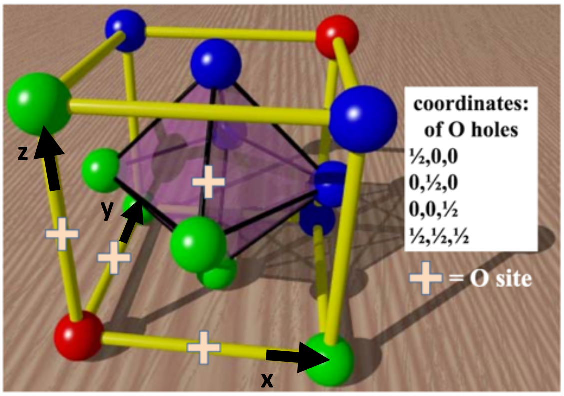
Answer: Percent volume taken up in ccp structure =

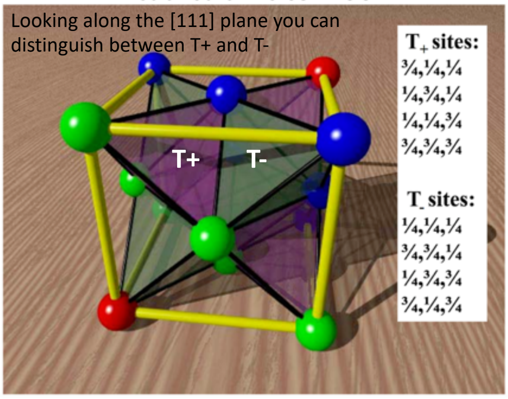
$$\frac{4*(4/3)\,\pi r^3}{16r^3\sqrt{2}} = 0.7405$$

As you know most solids are not made up of single atoms. So often there are secondary atoms for instance found in interstitial sites. There are two types of holes found in solid structures, tetrahedral sites and octahedral sites. For the tetrahedral sites There is T+ and T-. The plus or minus is dictated by the direction that the apex points if looking along the 111 direction (along the body diagonal).







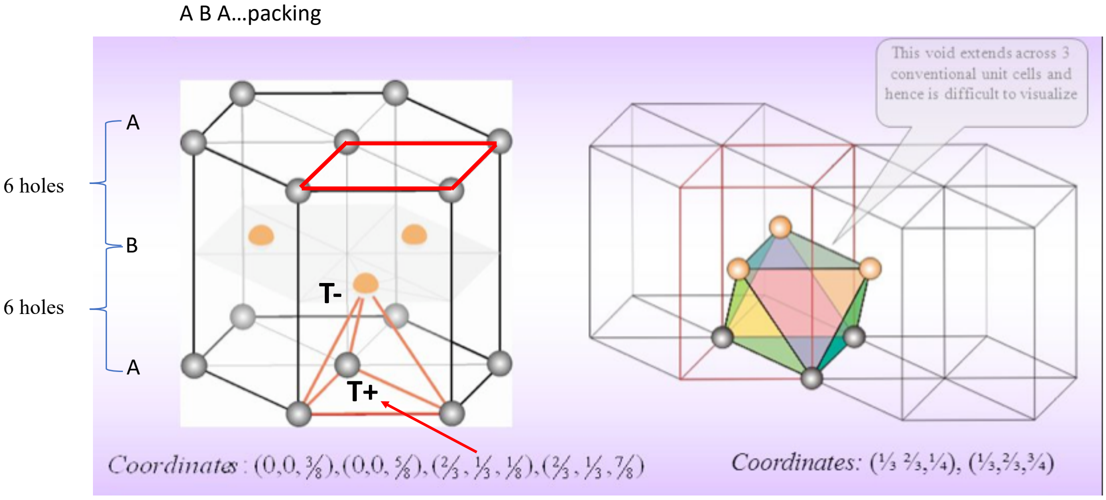


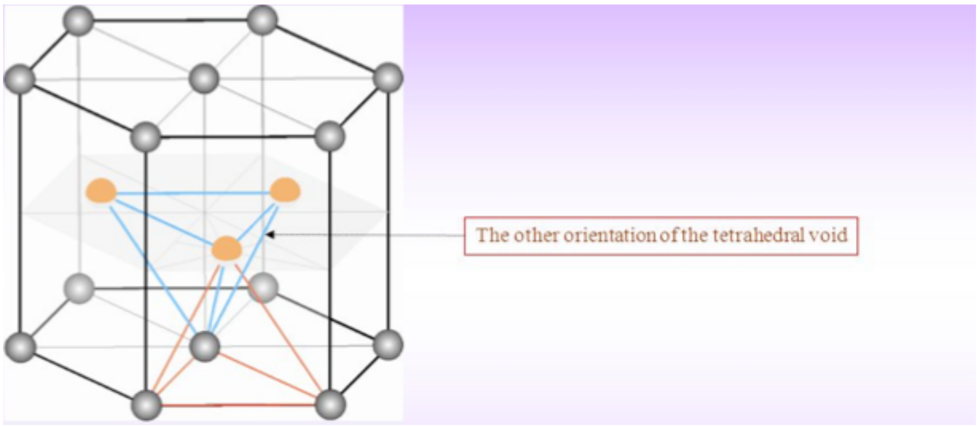
Note that for the octahedral holes there are only 4 coordinates but there are octahedral holes in the middle of all edges, but these are generated by the other surrounding unit cells. There is also one octahedral hole at the center of the unit cell.

Question: if we consider atoms in the middle of the edges and then one in the center, how many total atoms do we have if all octahedral holes are filled? How many tetrahedral holes?

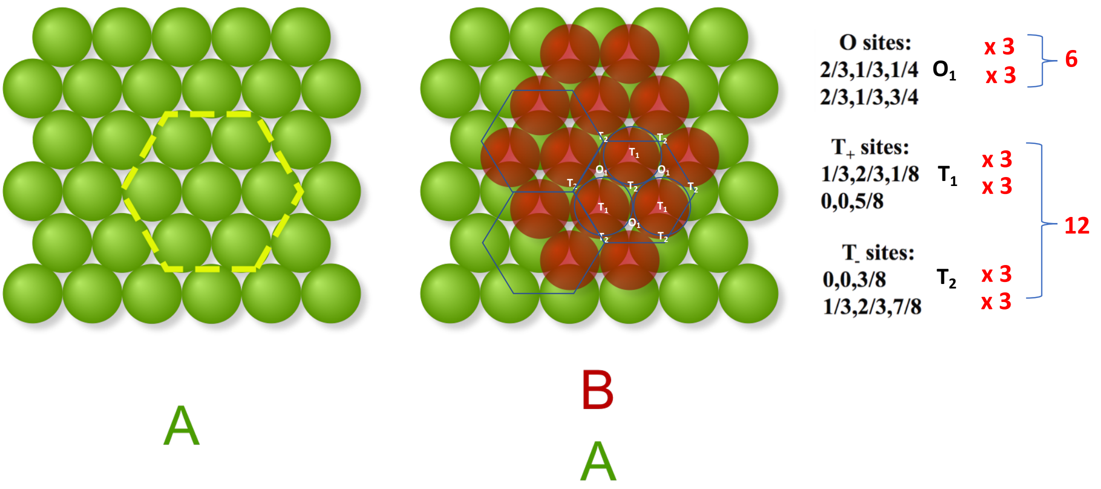
Answer: 4 octahedral and 8 tetrahedral

Intersticial sites in HCP There are 6 octahedral holes and 12 tetrehedral holes. There is of course a T+ and a T-.





And from a space filling model:



Most common structure types we should be able to describe at this point if we consider the type of packing, ccp or hcp and the location of the T and O holes. Here are the most important close packed structures.

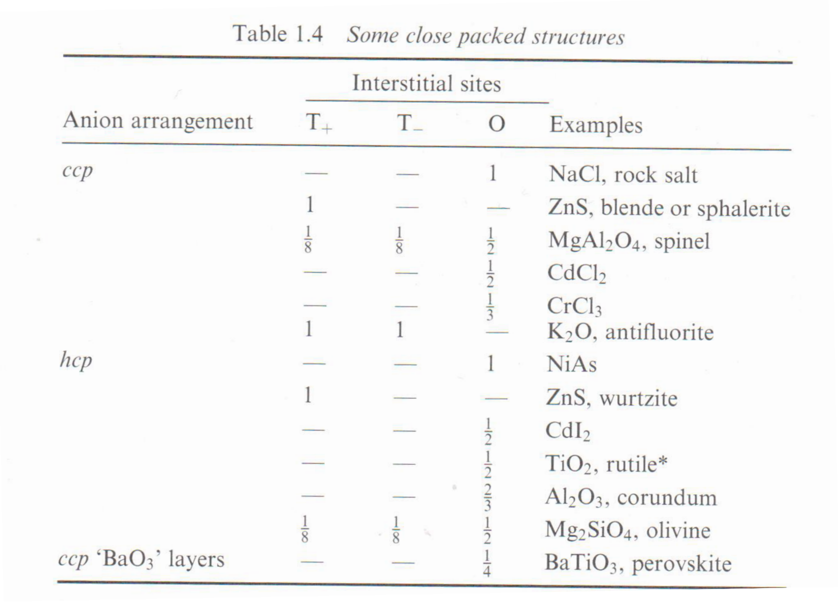


Table 1.4 *Some close packed structures*

	Interstitial sites			
Anion arrangement	T_+	T_-	O	Examples
ccp	—	—	1	NaCl, rock salt
	1	—	—	ZnS, blende or sphalerite
	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{2}$	$MgAl_2O_4$, spinel
	—	—	$\frac{1}{2}$	$CdCl_2$
	—	—	$\frac{1}{3}$	$CrCl_3$
	1	1	—	K_2O, antifluorite
hcp	—	—	1	NiAs
	1	—	—	ZnS, wurtzite
	—	—	$\frac{1}{2}$	CdI_2
	—	—	$\frac{1}{2}$	TiO_2, rutile*
	—	—	$\frac{2}{3}$	Al_2O_3, corundum
	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{2}$	Mg_2SiO_4, olivine
ccp 'BaO_3' layers	—	—	$\frac{1}{4}$	$BaTiO_3$, perovskite

In the next class your TAs will come in a build a few of these structures with you. There are structures that have cation arrays with anions filling the interstitial sites, like fluorite, where Ca has a ccp array and the F take up the tetrahedral holes.