L3: Introduction to crystal structures

Wednesday, July 29, 2020 8:30

Time on task: 1 hour (Material posted on August 31st, Office hour: Wednesday Sept 9th)

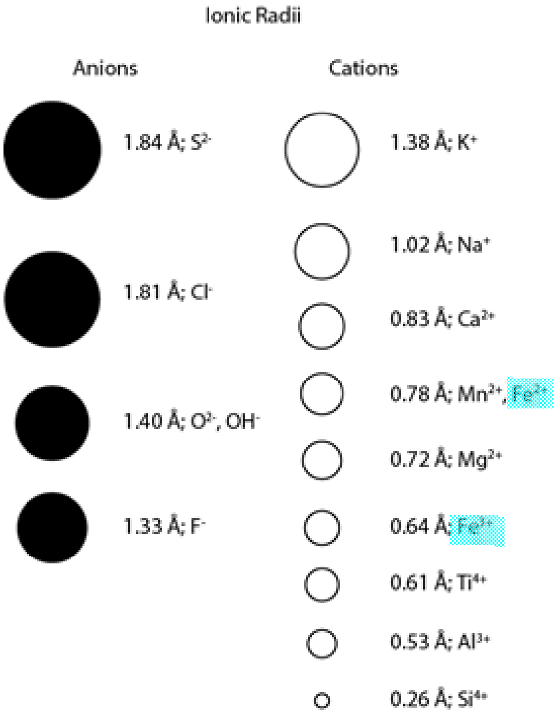
Goals:

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

1) Describe the arrangement of the anions and cations in a crystal structure
2) Determine the crystallographic site of a ions

This lecture is complemented with your lab #2 (due on Friday Sept 11th)

- For each type of atoms, we have an ionic radius that is a function of each element.

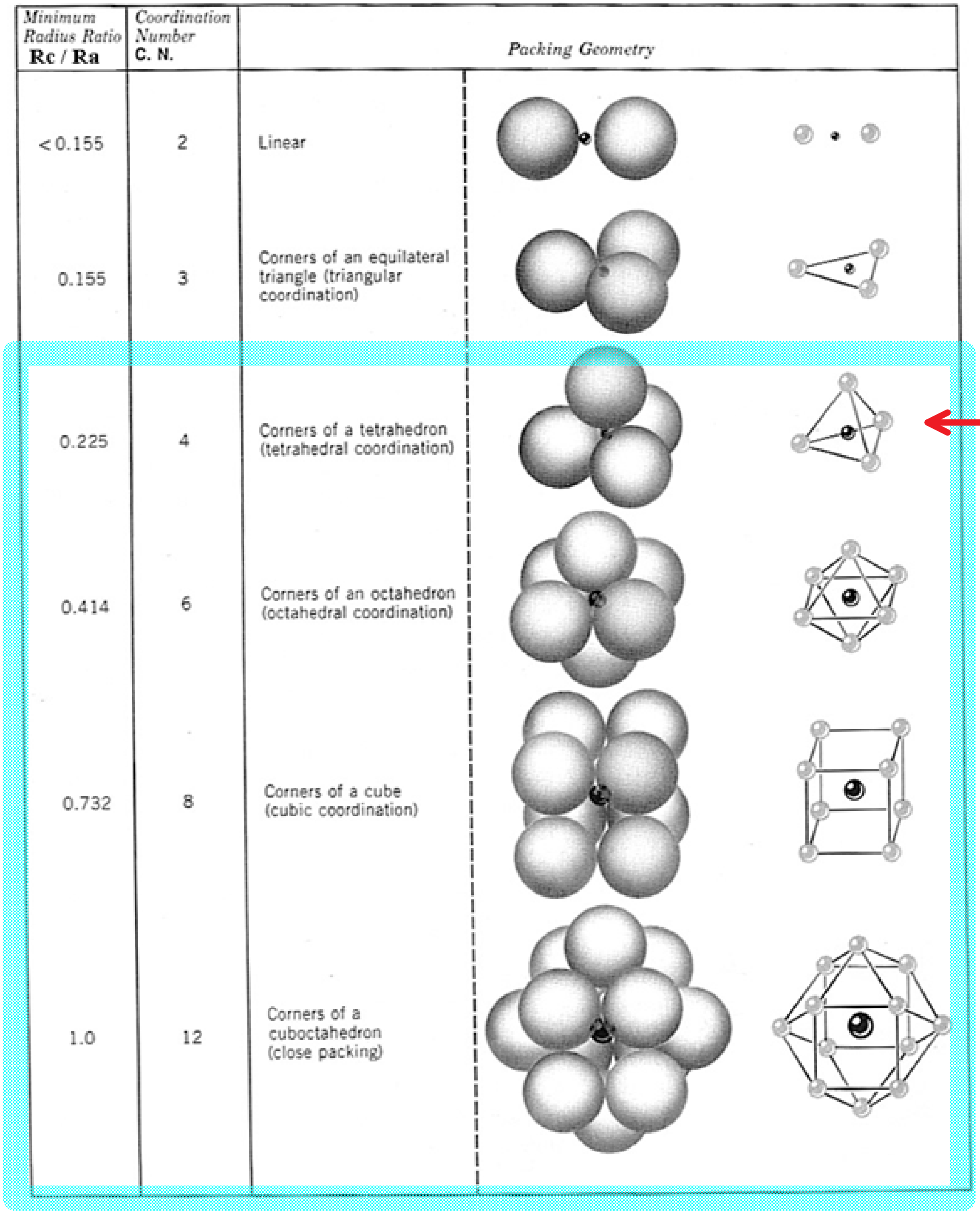


You can notice that Fe^{2+} (ferrous iron) does not have the same ionic radius than Fe^{3+} (ferric iron). The ionic radius depend on the **valency**.

Overall, for a given element, the radius decreases with increasing valency.
On the contrary, for a given valency, the ionic radius increase with the atomic number (and number of electrons) of the element.

Anions and cations have different sizes and valences and both will defined the way that they are organized in the crystal structure.
But in every crystal structure, void always try to be minimal.

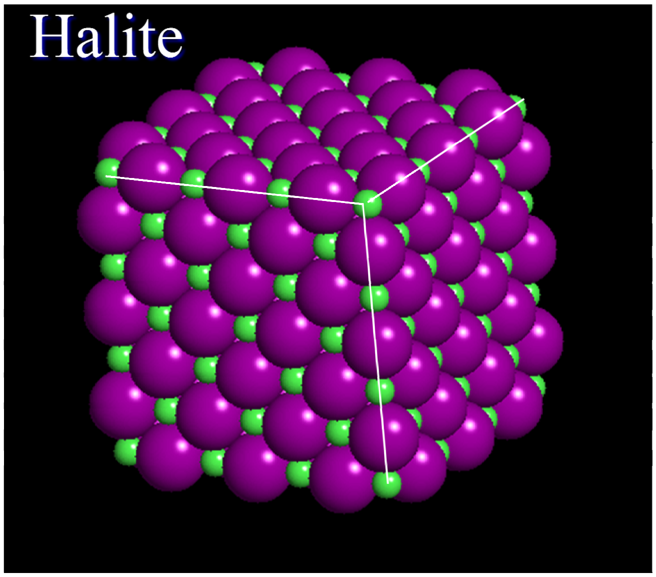
- **Definition.** **The coordination number or CN** is the number of closest neighbors of opposite charge around an ion. It can range from 2 to 12 in ionic structures. These structures are called coordination polyhedron. In practice, we always consider coordination of anions about a central cation.

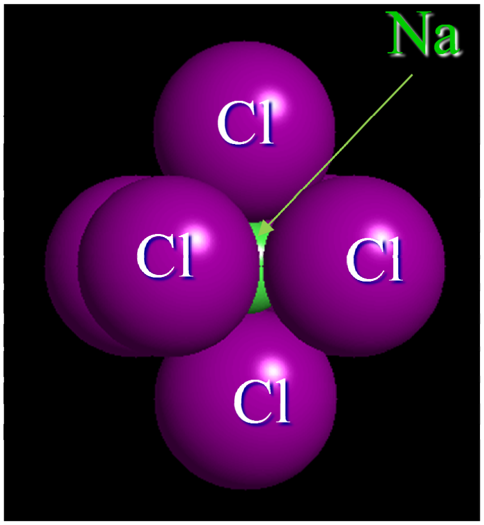


Minimum Radius Ratio **Rc / Ra**	*Coordination Number* **C. N.**	*Packing Geometry*
< 0.155	2	Linear
0.155	3	Corners of an equilateral triangle (triangular coordination)
0.225	4	Corners of a tetrahedron (tetrahedral coordination)
0.414	6	Corners of an octahedron (octahedral coordination)
0.732	8	Corners of a cube (cubic coordination)
1.0	12	Corners of a cuboctahedron (close packing)

Linear and triangular sites are however quite rare.
In this picture, the light gray spheres are the anions and the small black sphere are the cations. When all the anions are in contact, we call it "**close packing**".
The space available for the cation will not the same for each of these structures/polyhedra. Hence, the relative size of the ionic radii will control the CN.

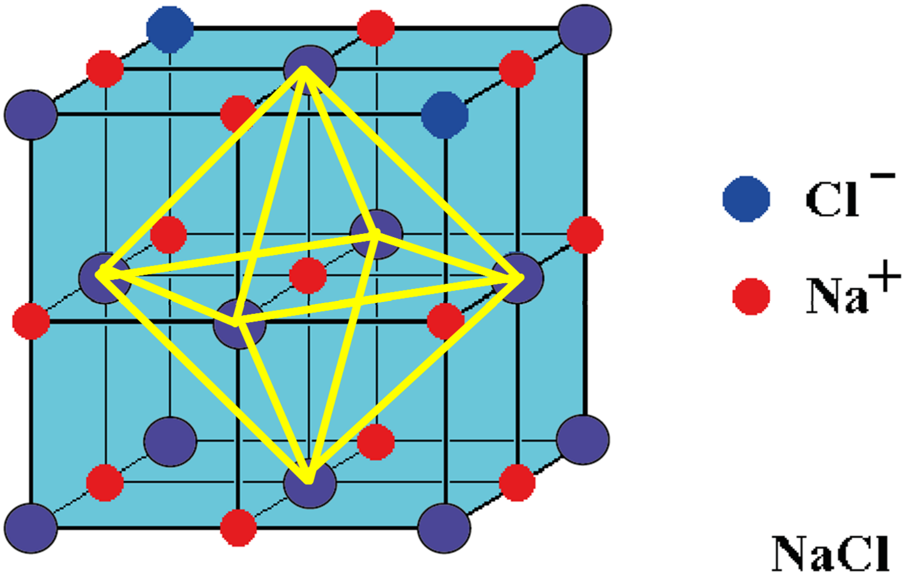
e.g., halite:





Na+ cations are in green, Cl- anions are in purple. Each Na+ is surrounded by 6 Cl-. The atoms of Cl- are in contact wih each other (close packing). Hence, the coordination polyhedra around Na+ is a octahedral coordination. The octahedral shape however is not always easy to visualize.

Hence, we often use a less realistic representation by "spacing" the atoms in the structure:



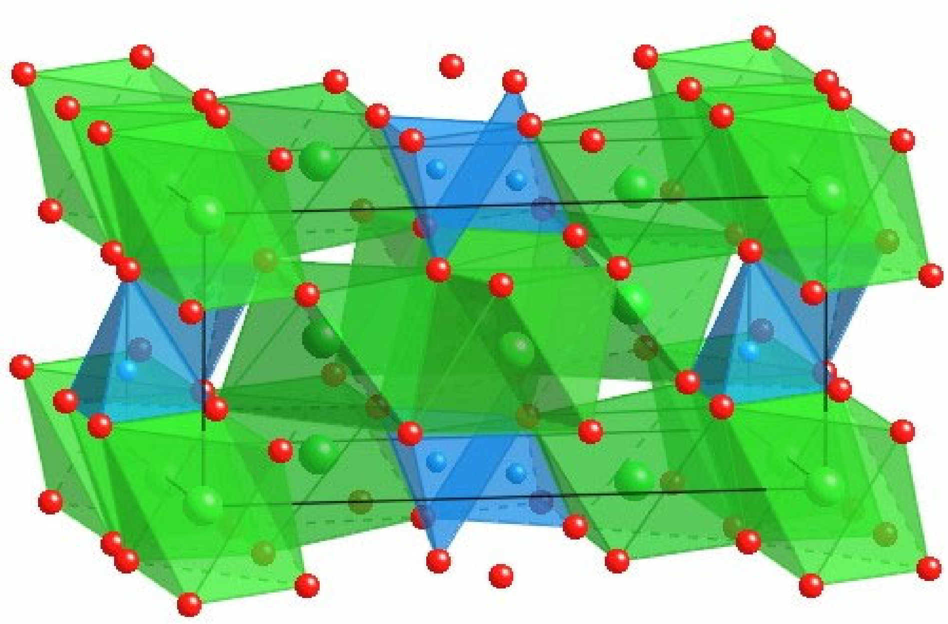
In this representation, anions Cl- are in blue and form the crystal lattice/unit cell. The cations Na+ are in red.

What type of unit cell do the anions form? What is the motif/base in this crystal structure?

As you can see, the cation located in the middle of the unit cell is surrounded by 6 Cl-. In yellow, I highlighted the shape of the coordination polyhedra. Coordination polydedra are called **crystallographic sites.**

We already see the tetrahedral sites in the previous lectures. In fact, silicates are classified as function of the arrangement of the silica tetrahedra (an atom of Si^{4+} surrounded by 4 atoms of O^{2-}) in the structure.

Start to familiarize yourself with the various crystallographic sites. e.g., Forsterite: Mg^{2+} are in octahedra sites (green), Si^{4+} are in tetrahedral sites (blue) (oxygen are represented in red).



Source: http://som.web.cmu.edu/structures/S086-forsterite.html

You can visualize this structure in 3D with **forsterite.html** posted on Canvas.

- To determine the CN of an ion, we look at the radius ratio: small ion/big ion. Hence, the maximal ratio is 1. In most cases, cations are smaller than anions, so we look at the ratio: R_{cation}/R_{anion}

R_{small}/R_{big}	C.N.	Type
1.0	12	Hexagonal or Cubic Closest Packing
1.0 - **0.732>=**	8	Cubic
<0.732 - 0.414	6	Octahedral
<0.414 - 0.225	4	Tetrahedral (ex.: SiO44-)
<0.225 - 0.155	3	Triangular
<0.155	2	Linear

What determine the CN is the **higher limit**.

e.g., a structure with a radius ratio of 0.414 will show a CN=6 (octahedral site).

For the elements that occur in common minerals in the Earth's crust, the most common coordinating anion is Oxygen (O^{2-}). The following table gives the ionic radius and coordination of these common cations coordinated with oxygen:

cation	C.N. (with Oxygen)	Coord. Polyhedron	Ionic Radius, Å
K^+	8 - 12	cubic to closest	1.51 (8) - 1.64 (12)
Na^+ Ca^{+2}	8 - 6	cubic to octahedral	1.18 (8) - 1.02 (6) 1.12 (8) - 1.00 (6)
Mn^{+2} Fe^{+2} Mg^{+2} Fe^{+3} Ti^{+4} Al^{+3}	6	Octahedral	0.83 0.78 0.72 0.65 0.61 0.54
Al^{+3} Si^{+4} P^{+5} S^{+6}	4	Tetrahedral	0.39 0.26 0.17 0.12
C^{+4}	3	Triangular	0.08

Note that some cations (and anions) can present different ionic radius (e.g., Al3+), and, consequently, might sit in different types of sites (e.g., octahedral versus tetrahedral).

This is because the ionic radius (and the coordination number) can also be affected by the environment (i.e., other ions and site present in the structure.

4.1 Pauling's rules.

Linus Pauling studied crystal structures and the types of bonding and coordination that occurs within them. His studies found that crystal structures obey the following rules, now known as **Pauling's Rules**.

Linus Pauling

- **Rule 1**

Around every cation, a coordination polyhedron of anions forms, in which the cation-anion distance is determined by the radius sums, and the coordination number is determined by the radius ratio.

This rule simply sets out what we have discussed above, stating that the different types of coordination polyhedra are determined by the radius ratio, Rx/Rz, of the cation to the anion.

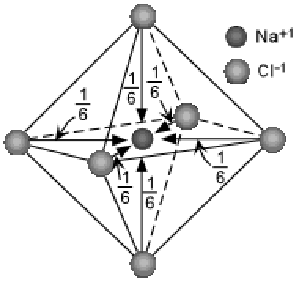
- **Rule 2, The Electrostatic Valency Principle**

The strength of an ionic (electrostatic) bond (electrostatic valency e.v.) between a cation and an anion is equal to the charge of the ion (z) divided by its coordination number (CN):

$e.v. = z/CN$

In a stable (neutral) structure, a charge balance results between the cation and its polyhedral anions with which it is bonded.

This second rule, while stated in a sort of complicated way, is quite intuitive.
For example, in NaCl each Na$^+$ is surrounded by 6 chlorine anions. Thus CN = 6 and e.v. = 1/6. So 1/6 of a negative charge reaches the Na ion from each Cl$^-$.
So the +1 charge on the Na ion is balanced by 6*1/6 =1 negative charge from the 6 Cl ions.

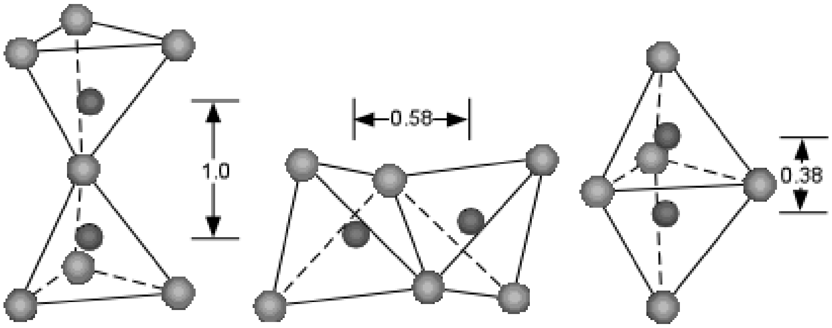


Similarly, in the CaF2 structure, each Ca+2 ion is surrounded by 8 F- ions in cubic or 8-fold coordination. The e.v. reaching the Ca ion from each of the F ions is thus 1/4. Since there are 8 F ions, the total charge reaching the Ca ion is 8*1/4 or 2.
So, again the charge is balanced.

- **Rule 3**

Shared edges, and particularly faces of two anion polyhedra in a crystal structure decreases its stability.

The reason for this is that sharing of only corners of polyhedra places the positively charged cations at the greatest distance from each other. In the example shown below, for tetrahedral coordination, if the distance between the cations in the polyhedrons that share corners is taken as 1, then sharing edges reduces the distance to 0.58, and sharing of faces reduces the distance to 0.38.



- **Rule 4**

In a crystal structure containing several cations, those of high valency and small coordination number tend not to share polyhedral elements.

Sharing of polyhedral elements for cations of high charge will place cations close enough together that they may repel one another. Thus, if they do not share polyhedral elements they can be better shielded from the effects of other positive charges in the crystal structure.

Rules 1 through 4 maximize the cation - anion attractions and minimize the anion-anion and cation-cation repulsions.

- **Rule 5: The Principle of Parsimony**

The number of different kinds of constituents in a crystal tends to be small.

This means that there are only a few different types of cation and anion sites in a crystal. Even though a crystal may have tetrahedral sites, octahedral sites, and cubic sites, most crystals will be limited to this small number of sites, although different elements may occupy similar sites.

4.2 Determination of CN_{anion}

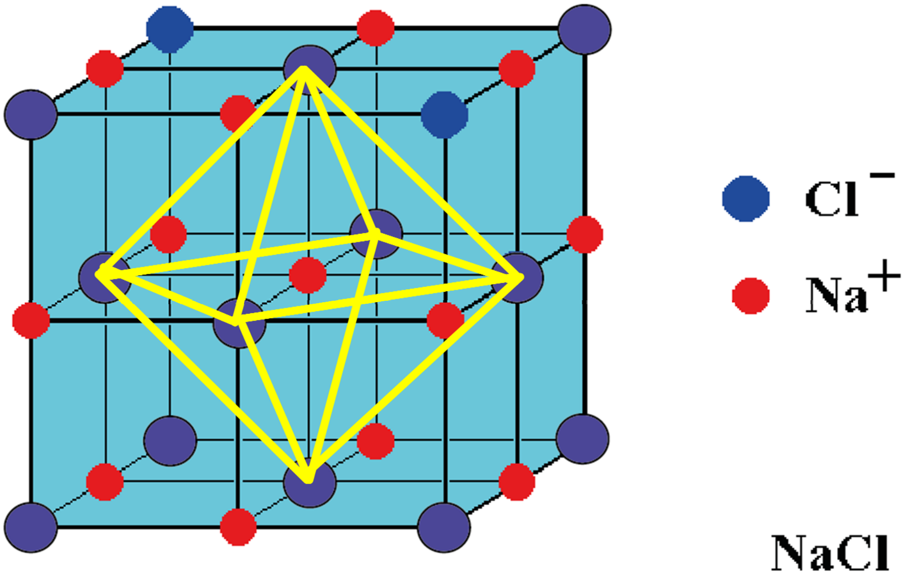
Cl- are also in octahedral sites.

$CN_{Cl} = 6$

When we try to define the **unit cell,** we usually look at the structure formed by the **anions** because they are bigger. The smaller cations wit try to fit in the holes between the anion. In the case of close-packing the anion touch each other.

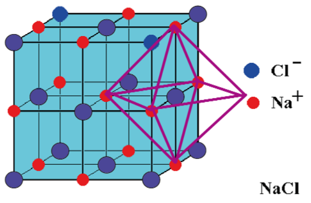
Let's look at a face-center cubic unit cell (fcc).

e.g., Halite:



As discussed above, the Na+ cations have a CN =6 are are sitting in octahedral sites.

Reminder: The coordination number or CN is the number of closest neighbors of opposite charge around an ion.
While we usually refer to the coordination polyhedron/crystallographic site around the cations, we could also describe the coordination polyhedron around the anions (i.e, the crystallographic site of the anion or, in other words, the number of cations around each anions).
The problem is because anions are often used as the structure of the unit cell, their coordination polyhedron is harder to visualize as it extends outside of the unit cell.



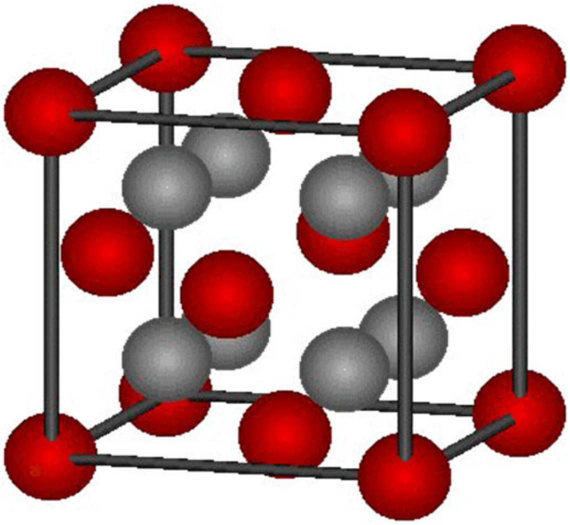
Rule: in any structure of formula A_xB_y, $CN_A/CN_B = y/x$

NaCl share this formula structure, so we can try applying the rule:
x=1, y=1: $1/1=1=CN_{Na}/CN_{Cl}$
$CN_{Cl} = CN_{Na}/1=6/1=6$
Using this rule, we calculate that the CN of Cl^- is 6.

So it's always a good way to double check your observations are correct.

We would say: "Cl and Na share the same type of arrangement (fcc) and the same type of crystallographic sites (octahedral, i.e., CN=6)."

Your turn! What are the types of arrangement and crystallographic site of Na (grey) and O (red) in antifluorite (Na_2O)?
(answer at the end of the personal assessment)



L3 - Personal assessment

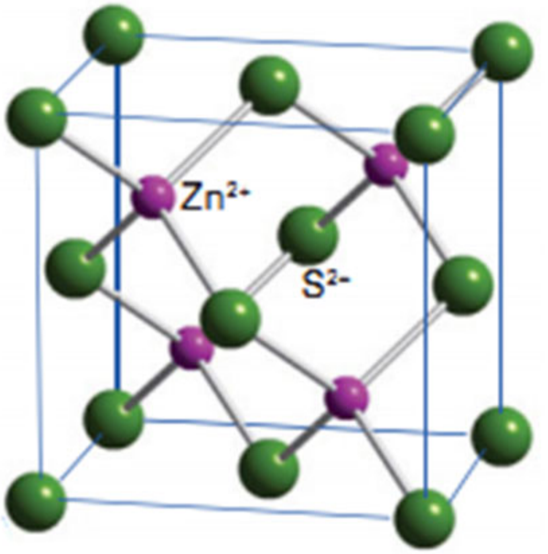
Wednesday, July 29, 2020 8:35

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

1) **Why do silica tetrahedra are isolated or only share corners in silicate structure?**

See Lecture 1 - part 3.1 for a review of the silica tetrahedra arrangements.
To visualize a silica tetrahedra in 3D and the various silica tetrahedra arrangements, open **SiO4.html** posted on Canvas-GEO3020-Lecture1-3D with your internet browser.

2) **What are the types crystallographic site of Zn (purple) and S (green) in spahlarite (ZnS)? What can you add regarding the crystallographic sites of Zn?**



Keys for antifluorite:
Cl has a fcc arrangement, while Na has a simple cubic arrangement.
Na atoms are in tetrahedral sites and O atoms are in cubic sites.
This is verified by $CN_{Na}/CN_O = 1/2$: $CN_{Na}=4$, CNO= $CN_{Na}*2/1=4*2=8$