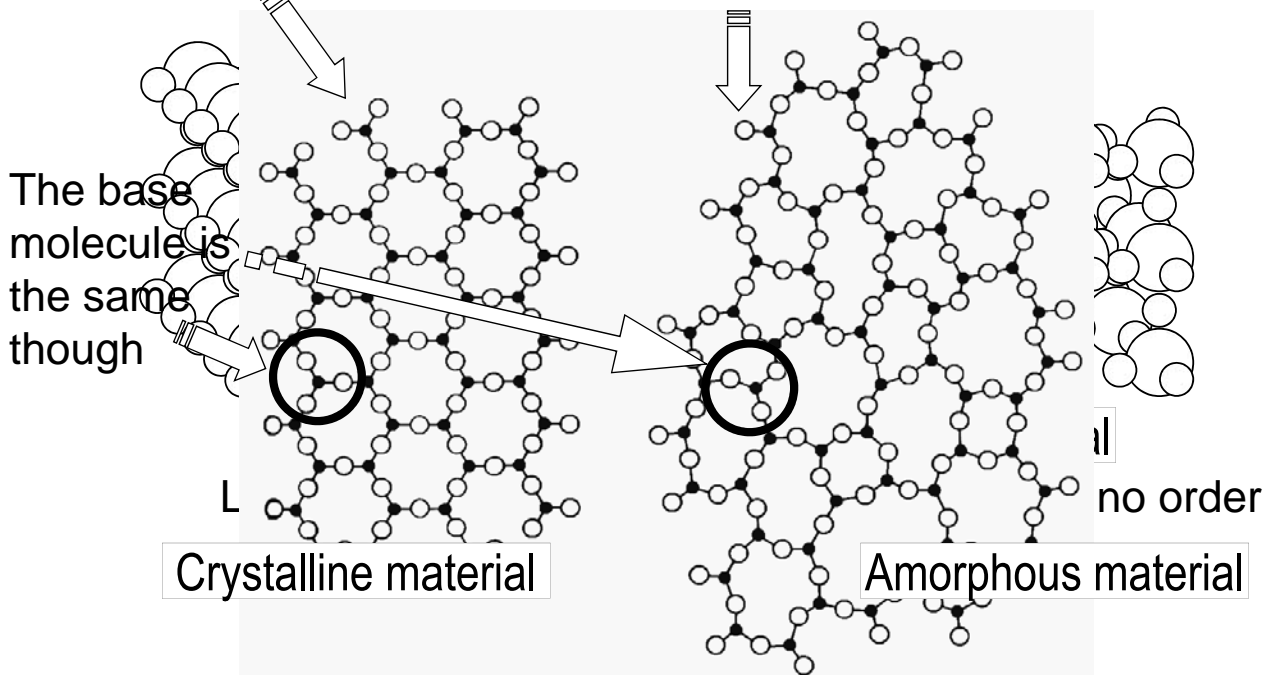


Chapter 3

The Structure of Crystalline Solids

The difference between crystalline and non-crystalline materials is in the extent of ordering

Both materials have the same composition but one is “ordered” and the other is “disordered”.



Some Properties of Amorphous Solids

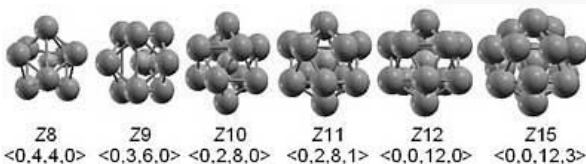
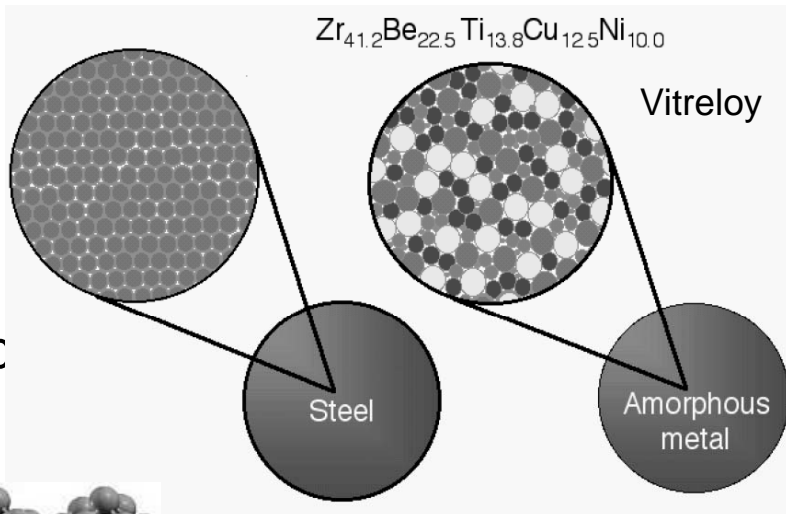
- Properties
- Solid lacks regular structures
- Has a melting range
- Restrictive movement of molecules
- Unable to identify unit cell in solid phase
- Breaks in random pieces

Examples: glass, some polymers, nylon

Read the *Inorganic Glasses* topic in pages 544-550

Amorphous Metallic Alloys or Metallic Glasses

- There are metallic amorphous solids (glasses).
- They have several special properties such as high elastic with high modulus.



In reality, metallic glasses have a short-range order. An atom becomes the center of a Kaster polyhedra.



Crystalline Materials

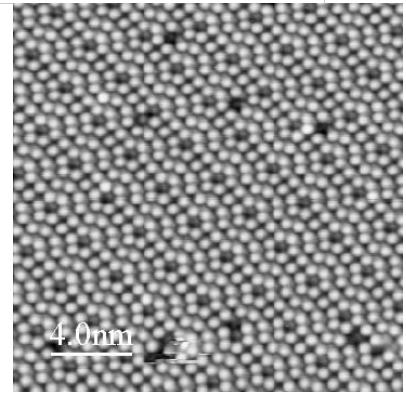
Atoms arranged in patterns called crystals. Crystalline solids have dense, ordered packed structures with lower bonding energies than amorphous solids.

The smallest repetitive volume which contains the complete lattice pattern of a crystal is called **unit cell**.

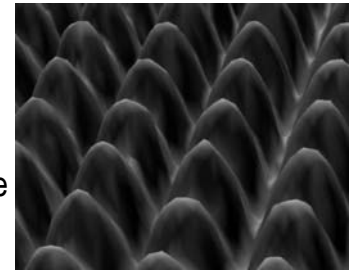
Size and shapes of a unit cell can be described by:

lattice constants

interaxial angles

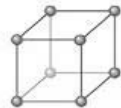


Scanning tunneling probe image of pure silicon (atomic resolution).

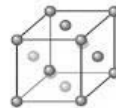


Scanning tunneling probe image of pure platinum surface

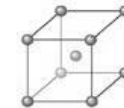
The 14 Bravais Lattices



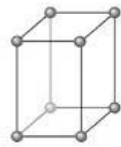
Simple cubic



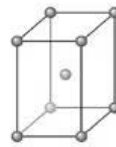
Face-centered cubic



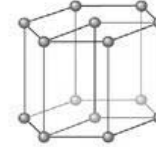
Body-centered cubic



Simple tetragonal



Body-centered tetragonal



Hexagonal



Simple orthorhombic



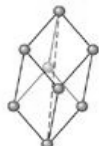
Body-centered orthorhombic



Base-centered orthorhombic



Face-centered orthorhombic



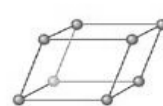
Rhombic



Simple monoclinic

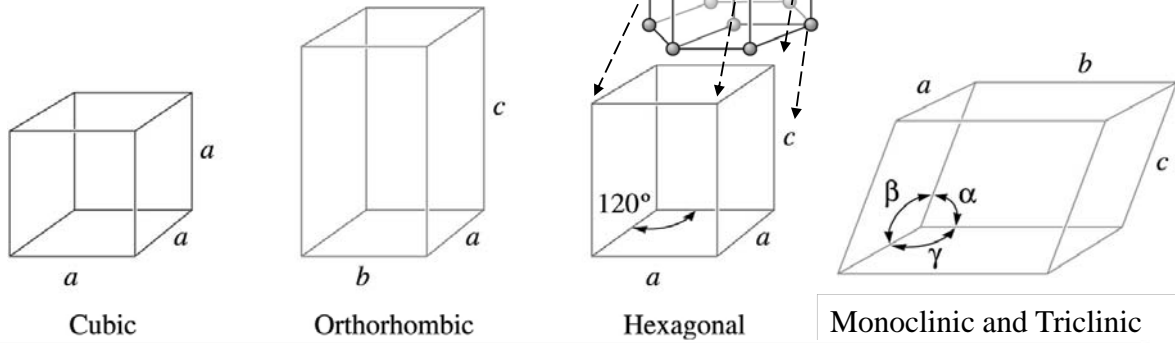


Base-centered monoclinic



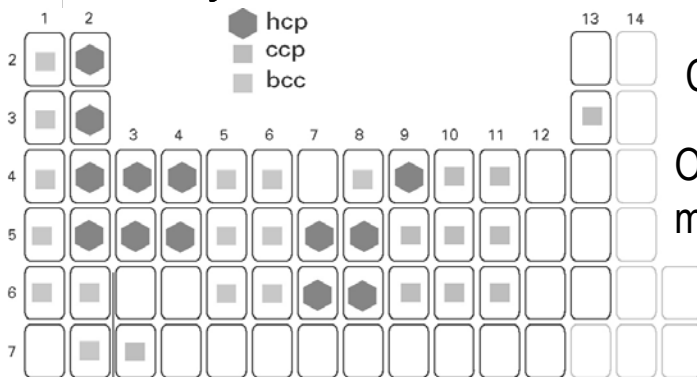
Triclinic

Definition of *lattice parameters* and interaxial angles for all crystal systems



Structure	Axes	Angles between Axes	Volume of the Unit Cell
Cubic	$a = b = c$	All angles equal 90°	a^3
Tetragonal	$a = b \neq c$	All angles equal 90°	a^2c
Orthorhombic	$a \neq b \neq c$	All angles equal 90°	abc
Hexagonal	$a = b \neq c$	Two angles equal 90° . One angle equals 120° .	$0.866a^2c$
Rhombohedral or trigonal	$a = b = c$	All angles are equal and none equals 90°	$a^3 \sqrt{1 - 3 \cos^2 \alpha + 2 \cos^3 \alpha}$
Monoclinic	$a \neq b \neq c$	Two angles equal 90° . One angle (β) is not equal to 90°	$abc \sin \beta$
Triclinic	$a \neq b \neq c$	All angles are different and none equals 90°	$abc \sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma}$

Crystal Structures in the Periodic Table



CCP is the same as FCC

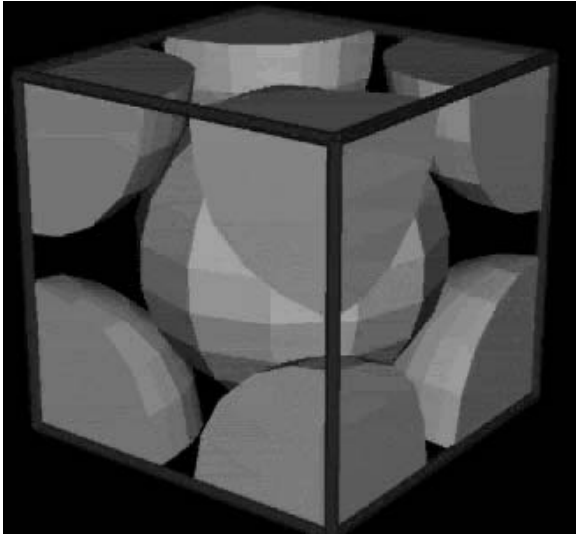
Other elements left blank have more complex structures



Exercise

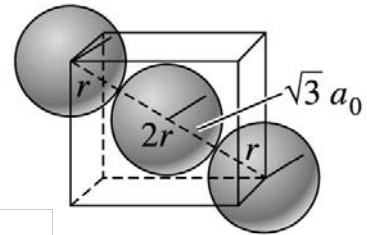
- Determine the volume of each unit cell as a function of the lattice parameters and the interaxial angles
- Determine the CN of each atom in the cubic, tetragonal and orthorhombic cells.
- Calculate the number of atoms included in each unit cell based on the concept shown in the next slide

Let's start with the BCC unit cell



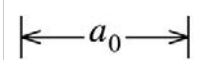
How many atoms in a BCC unit cell?

If all the atoms are identical (pure element) then we can write an equation relating a_0 and r :

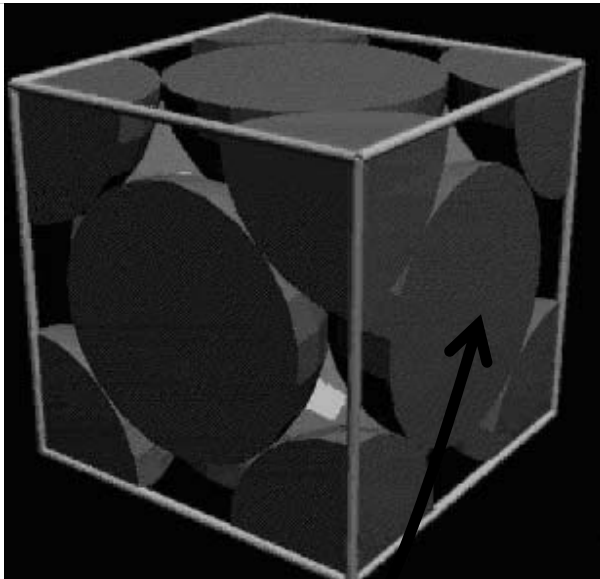


What's the CN of the central atom?

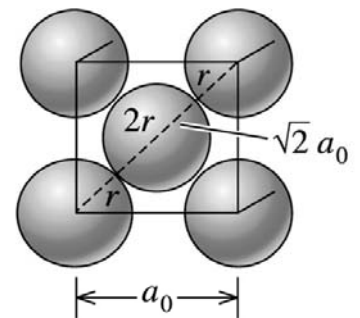
$$4r = \sqrt{3} \cdot a_0$$



Let's play with the FCC unit cell



How many atoms in an FCC unit cell?



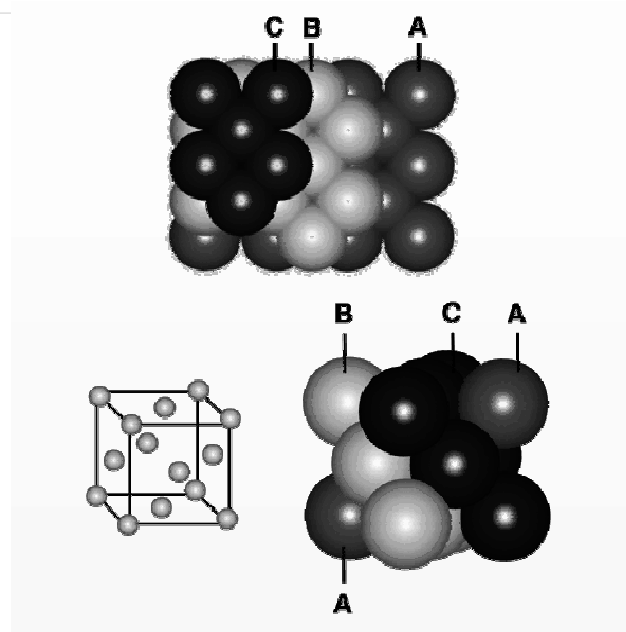
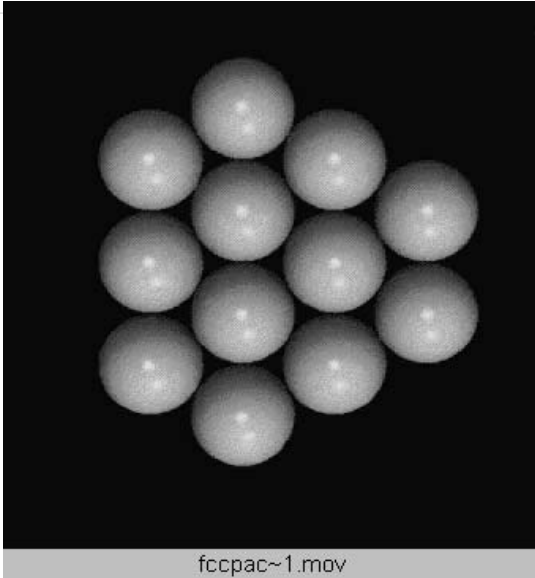
If all the atoms are identical (pure element) a_0 relates to the radius r :

$$4r = \sqrt{2} \cdot a_0$$

Coordination number of the central interstice?

CN of this atom?

FCC Packing Sequence ABCABC



Atomic Packing Factor APF

$$APF = \frac{\text{Volume of atoms in unit cell}}{\text{Volume of unit cell}}$$

Exercise: Give an expression for the APFs of:

a) a BCC crystal

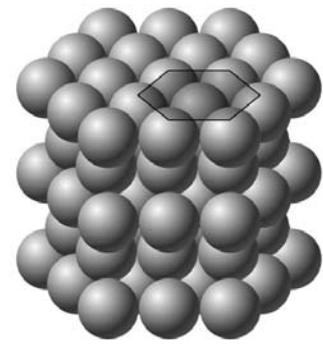
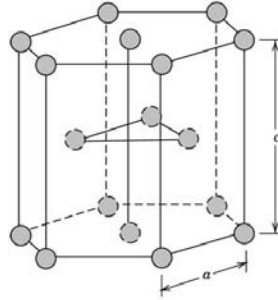
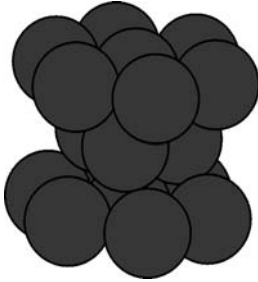
$$APF_{\text{BCC}} = \frac{2 \cdot \left(\frac{4\pi r^3}{3} \right)}{a^3} = \frac{2 \cdot \left(\frac{4\pi r^3}{3} \right)}{\left(\frac{4r}{\sqrt{3}} \right)^3} = \frac{\pi\sqrt{27}}{24} = 0.68$$

r³ cancels out

b) an FCC crystal

c) a BCT crystal (note that r, a, and c are independent)

The HCP unit cell



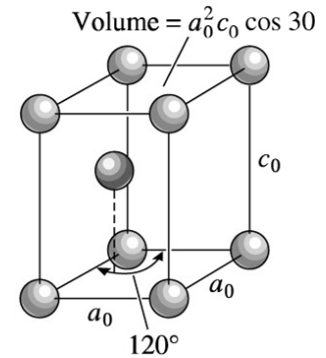
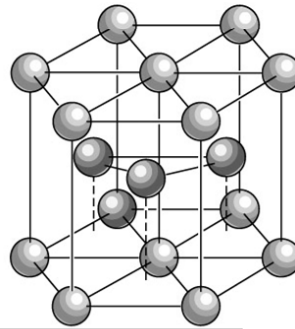
So, how many atoms are there in an HCP unit cell?

What is the relation between a_0 and r ?

In an *ideal* HCP unit cell a_0 is a function of c :

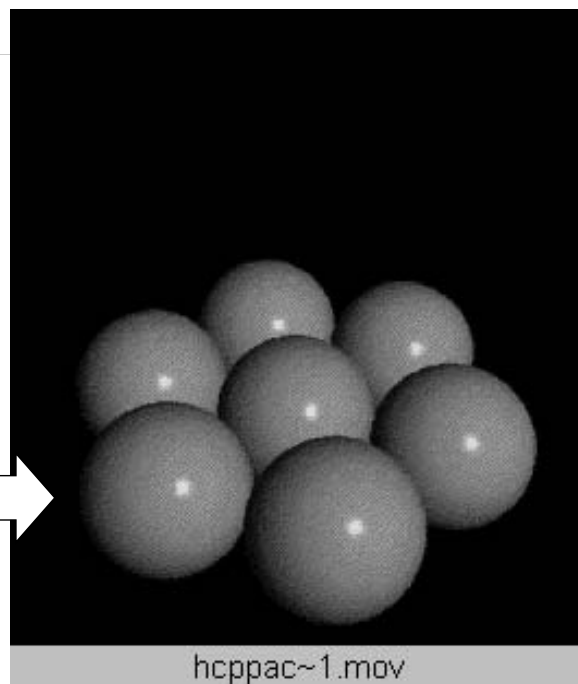
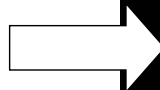
$$\left(\frac{c}{a}\right) = 2\sqrt{\frac{2}{3}}$$

← PROVE IT!!!!



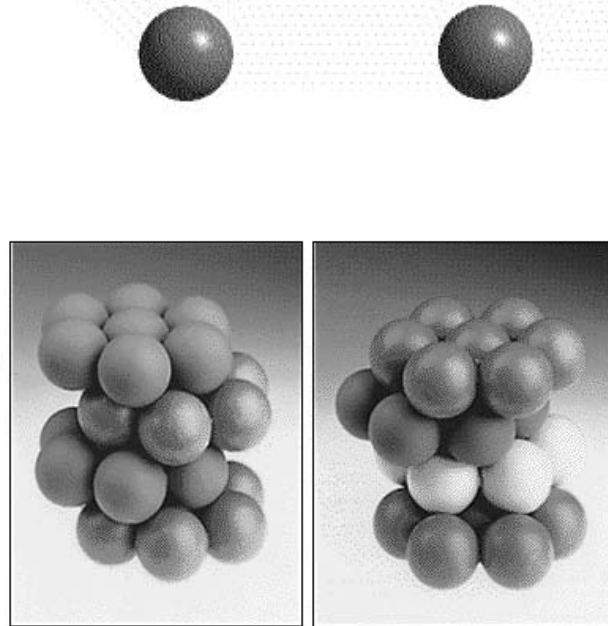
This is how the HCP stacking sequence ABABAB works

Start with the basal plane



This is what is different between both HCP and FCC stacking sequences

Notice the different positions in the tetrahedral sites. Try this at home with marbles. By the way, what is the coordination number of both central atoms? How about the other atoms?



HCP Crystal APF

Homework: Calculate the APF of an “ideal” HCP crystal. Then compare it with the APF of the BCC and FCC crystals.

Hint: you may want to play with marbles to complete this task. Pile them up and try to figure out the geometry. Also remember that the lattice parameter $a_0 = 2r$ for this crystal.

Summary

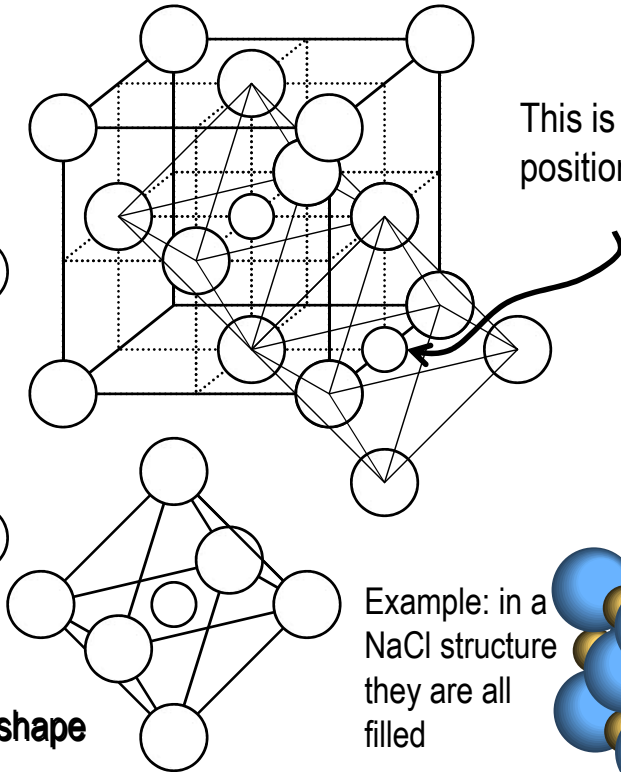
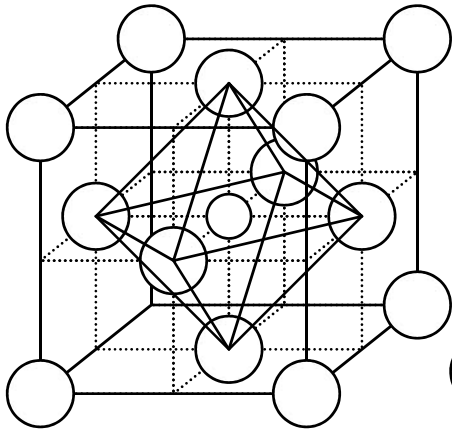
Structure	a_0 versus r	Atoms per Cell	Coordination Number	Packing Factor	Examples
Simple cubic (SC)	$a_0 = 2r$	1	6	0.52	Polonium (Po), α -Mn
Body-centered cubic (BCC)	$a_0 = 4r/\sqrt{3}$	2	8	0.68	Fe, Ti, W, Mo, Nb, Ta, K, Na, V, Zr, Cr
Face-centered cubic (FCC)	$a_0 = 4r/\sqrt{2}$	4	12	0.74	Fe, Cu, Au, Pt, Ag, Pb, Ni
Hexagonal close-packed (HCP)	$a_0 = 2r$ $c_0 \approx 1.633a_0$ <i>ideal</i>	2	12	0.74	Ti, Mg, Zn, Be, Co, Zr, Cd



**More on coordination numbers:
Octahedral sites (interstices) have CN=6**

In FCC:

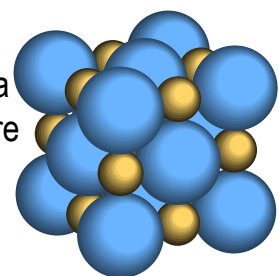
- Center $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
- Edges $(0, 0, \frac{1}{2}), (0, \frac{1}{2}, 0), (\frac{1}{2}, 0, 0)$
- 4 per unit cell



This is the $(\frac{1}{2}, 1, 0)$ position

8-sided shape

Example: in a NaCl structure they are all filled

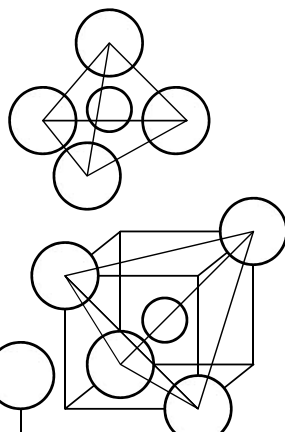
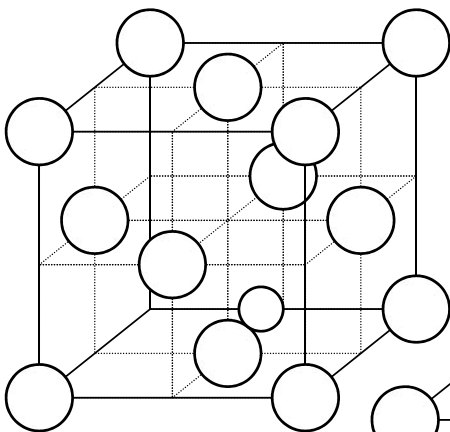


Periodic Table

INGE 4001 - Engineering Materials

Tetrahedral sites (CN=4) in an FCC unit cell

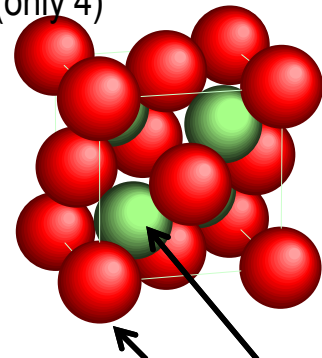
- Divide cell into 8 boxes - center of small box
- $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}), (\frac{3}{4}, \frac{1}{4}, \frac{1}{4}), (\frac{1}{4}, \frac{3}{4}, \frac{1}{4}), (\frac{3}{4}, \frac{3}{4}, \frac{1}{4}), (\frac{1}{4}, \frac{1}{4}, \frac{3}{4}), (\frac{3}{4}, \frac{1}{4}, \frac{3}{4}), (\frac{1}{4}, \frac{3}{4}, \frac{3}{4}), (\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$
- 8 per unit cell



4-sided shape

Analogous to the silicon tetrahedron

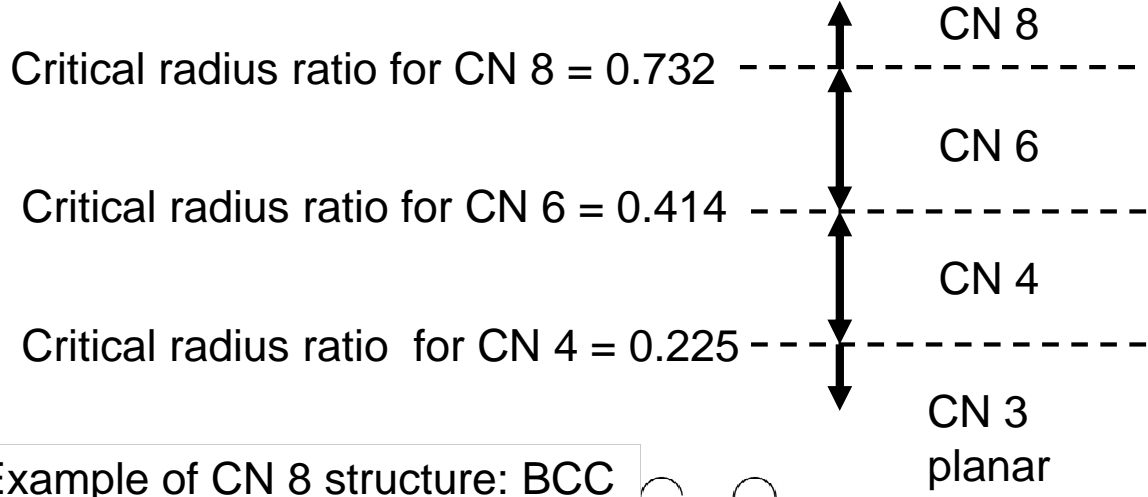
Example: GaAs has half-filled tetrahedral sites (only 4)



Ga⁺³ As⁻³

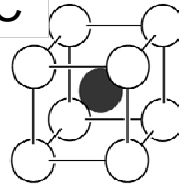
More on Radius Ratio Rules and CN

Critical radius is size of atom which just fits in site
 Define minimum for bonding (*i.e.* atoms must touch to bond)



Example of CN 8 structure: BCC

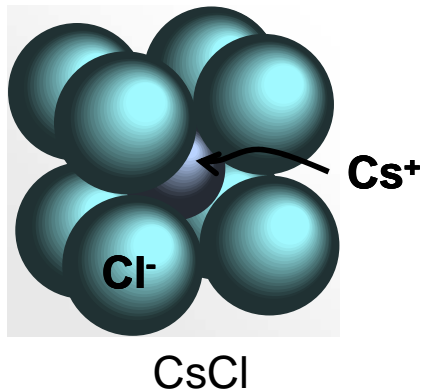
0.732–1.000



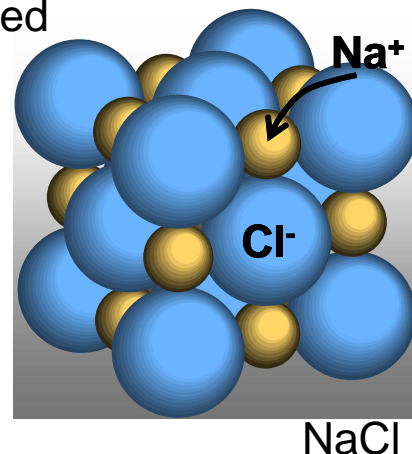
An overview of more ionic and covalent crystals

First, the definition of crystal prototype

Simple cubic with a CN 8 ion



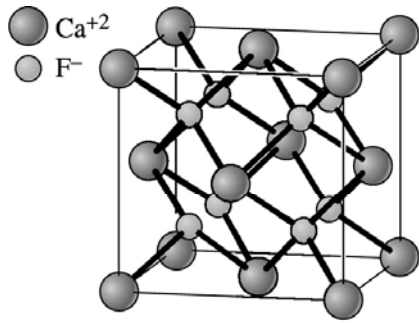
Rock salt type structure: FCC with all octahedral sites (CN 6) occupied



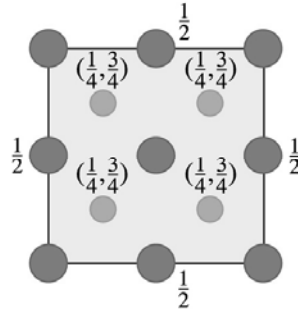
Homework: investigate other ionic crystals with these two structures.

More compounds...

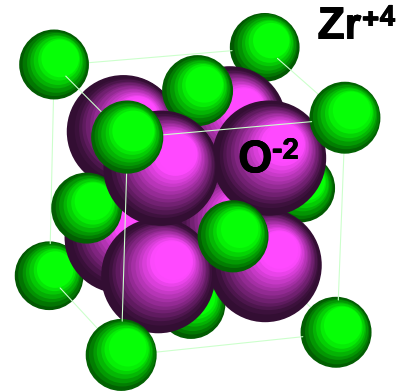
The fluorite (CaF_2) type structure is an FCC cell with all tetrahedral sites (CN 4) filled



Fluorite cell



Plan view



Example:
zirconia ZrO_2

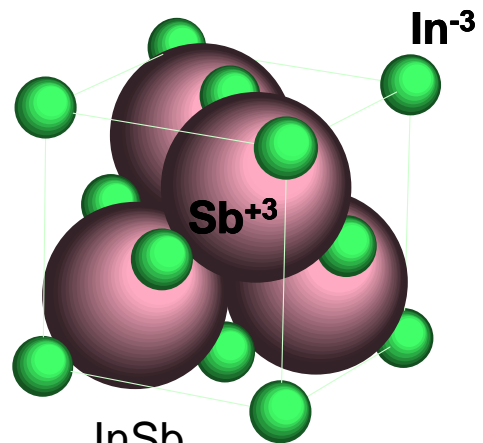
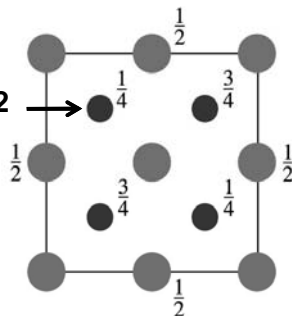
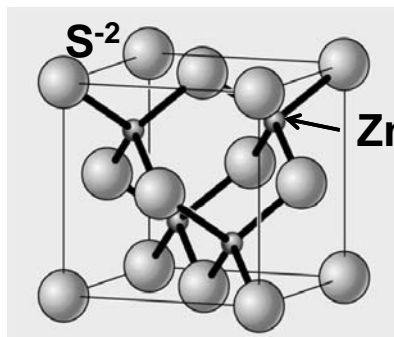
Note of the positions of the four inner ions (green)

In *antifluorite* type crystals, the positions of cations and anions is reversed

Homework: Find other compounds with fluorite type structures

More compounds...

The zinc blende (ZnS) type structure is an FCC cell with the tetrahedral sites (CN 4) half-filled

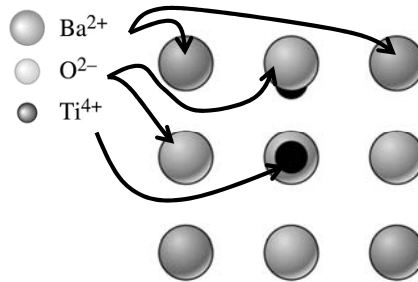
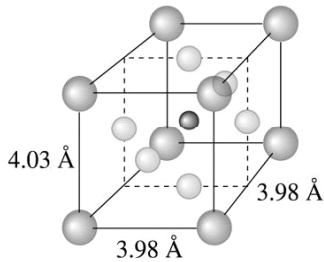


Take careful note of the positions of the four inner Zn cations (red)

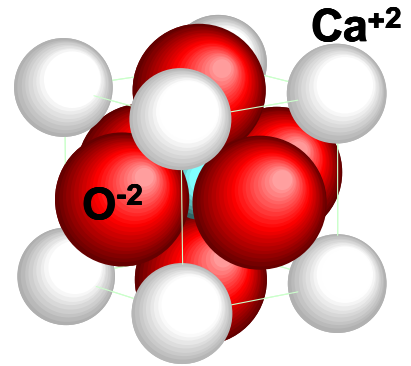
Homework: Find other zinc blende type structures (look at semiconductors)

Perovskite type structures

Barium titanate cell is a variant with a slight lack of symmetry (tetragonal) that creates a slight charge unbalancing.



Perovskite: plan view



Another example:
calcium titanate
 CaTiO_3

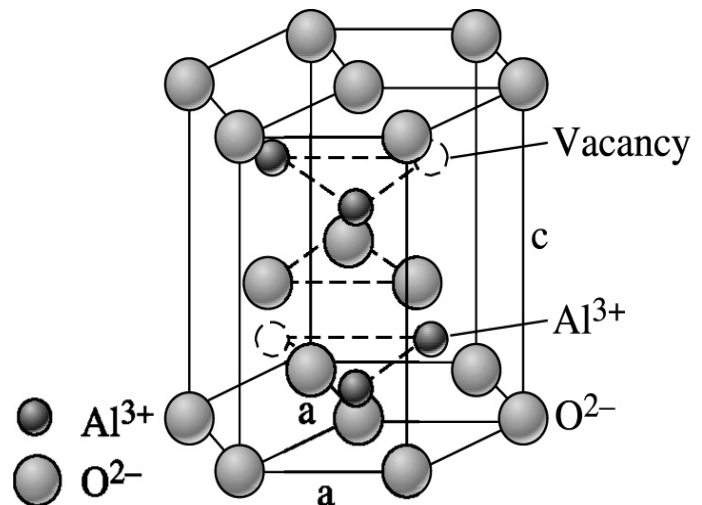
The crystal becomes polarized. If we try to remove the lack of symmetry, the material resists with a force \rightarrow *piezoelectricity*

Hexagonal Structures

Note the positions of the Al^{3+} ions in $\alpha\text{-Al}_2\text{O}_3$ (Corundum). They are located in octahedral sites (only 4 out of 6 available)

This can also be consider a rhombohedral unit cell

Homework: Find other corundum type structures (look at insulators)



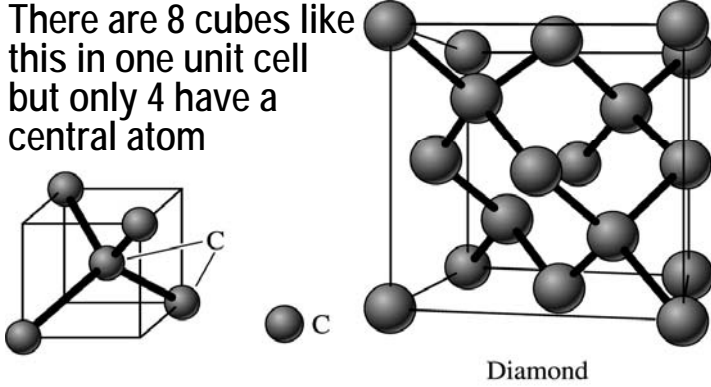
Homework:

Study carefully the wurzite structure and compounds with this type of structure.

Diamond Cubic Structure and Derivatives

Group IVA elements (diamond, Si, Ge, α -Sn) are examples due to their valence 4 and covalent bonds

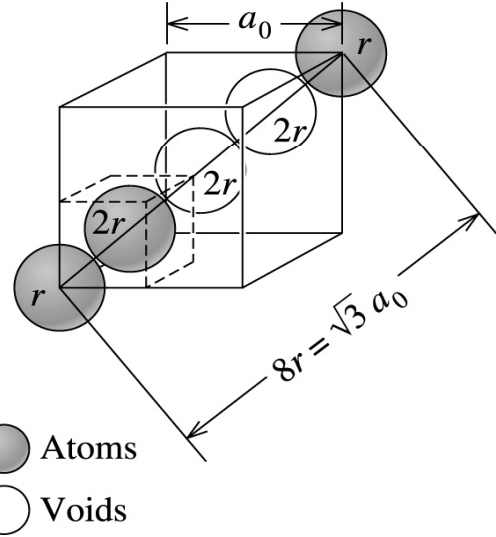
There are 8 cubes like this in one unit cell but only 4 have a central atom



Determine the exact positions of all atoms

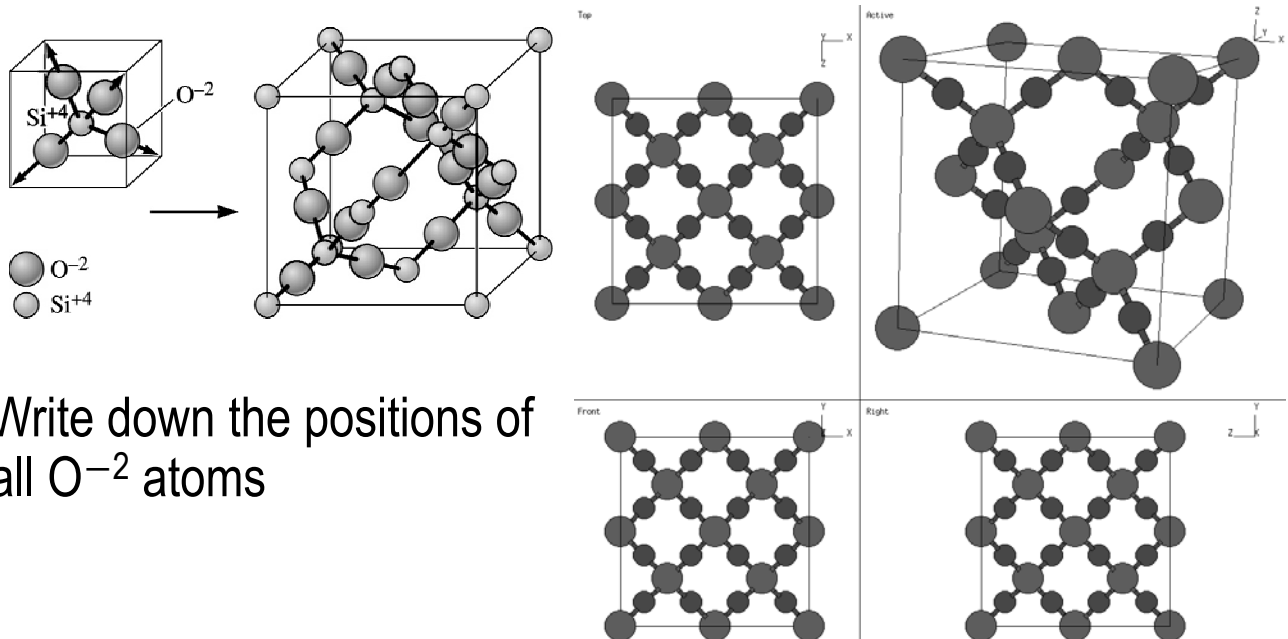
The relation between the lattice parameter a_0 and r is:

$$8r = \sqrt{3} \cdot a_0$$



Diamond Cubic Structure and Derivatives

SiO_2 (silica) can form β -cristobalite



Write down the positions of all O^{-2} atoms

