Crystals, packings etc.

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These notes complement chapter 6 of Anderson, Leaver, Leevers and Rawlings

Bond Distances

We have seen that in the P-cubic structure, the cell parameter $a = 2r = d$ where r is the radius of an atom. If two atoms touch, the distance between their centers — the bond distance (or length) — corresponds to the sums of their radii. Therefore:

- In the primitive cubic structure $d = 2r = a$.
- In the I-cubic structure, $\sqrt{3}a = 4r$ so that the bond distance is $d = 2r = \sqrt{3}/2a$
- In the F-cubic structure, $\sqrt{2}a = 4r$ so that the bond distance is $d = 2r = a/\sqrt{2}$.

We can compare bond lengths in fcc Ni ($a = 3.524$ Å, $d = 2.492$ Å) and bcc Fe ($a = 2.8665$Å, $d = 2.4825$ Å). We find that they are very similar as we might expect for two elements that are nearly neighbors.

Densitites

If the cubic unit cell has the side a, its volume is $V = a^3$. If we know the cell parameter, and the name of the element within the unit cell, we can calculate the density of the material precisely.

As an example, consider Ni, in fcc Ni, where $a = 3.524$ Å. We have $V = a^3 = (3.524\text{Å})^3 = (3.524 \times 10^{-8}\text{cm})^3 = 4.376 \times 10^{-23}\text{cm}^3$

The atomic mass of Ni is 58.693 so one Ni atom weighs ($58.693/6.023\times10^{23}$) g = 9.7448×10^{-23} g. There are four Ni atoms per unit cell so that the density ρ is given by

$$\rho = \frac{\text{mass}}{\text{volume}} = \frac{4 \times 9.745 \times 10^{-23}\text{g}}{4.376 \times 10^{-23}\text{cm}^3} = 8.907\text{g cm}^{-1}$$

We can perform other, similar calculations where the unknown is different.

Number of neighbors

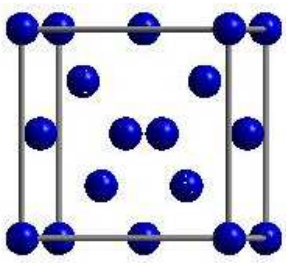
In the P-cubic structure, each atom has 6 nearest neighbors, in I-cubic, the number is 8, and in F-cubic, the number is 12.

More complex elemental structures

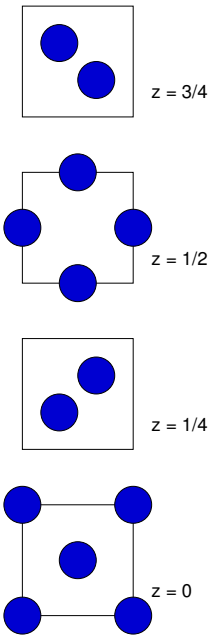
More complex structrures than the four we have mentioned (P-cubic, I-cubic, F-cubic and hexagonal close-packed[1]) We will start with the diamond structure that is adopted by C (diamond), Si etc.

[1] We will return to a discussion of this structure presently

Diamond

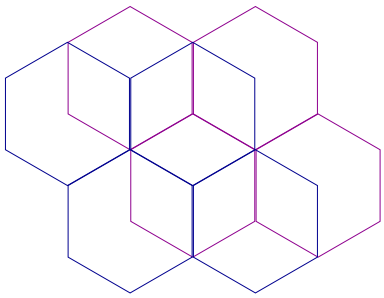


This structure can be built up from the fcc structure by inserting some extra layers.

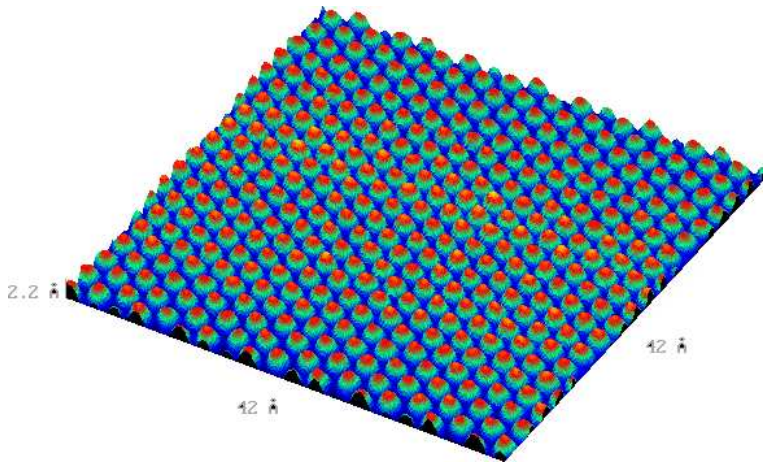


Note that the layer at $z = 1$ is identical to $z = 0$ and is not shown. Also note that $z = 0$ and $z = 1/2$ are identical to fcc. The cell parameter of Si is $a = 5.4309$ Å. For carbon (diamond) it is $a = 3.56780$ Å. The packing fraction/efficiency is only 0.34.

Graphite



And here is an image of the top surface using a technique called Scanning Tunnelling Microscopy (STM):

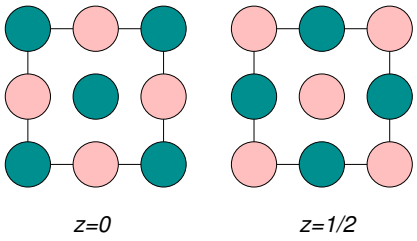


From: http://www.physics.louisville.edu/www/public/faculty/stm/

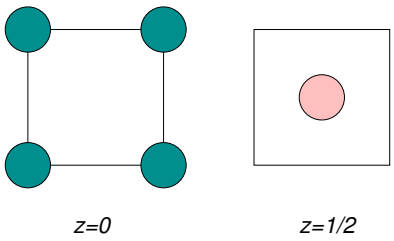
The structures of simple compounds

As we go to compounds, structures can become more complex. One of the simplest structures is that of common salt.

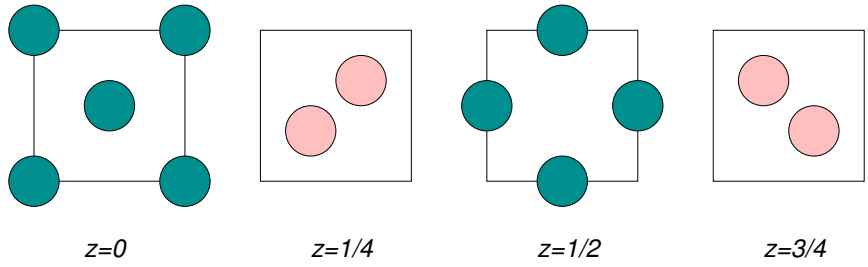
NaCl: Adopted by a number of halides, oxides, chalcogenides. Note that each cation has 6 neighbors and each anion has 6 neighbors etc. The cell parameter of NaCl itself has $a = 5.63$ Å. Other examples: AgCl, BaS, CaO, CeSe, DyAs, GdN, KBr, Lap, LiCl, LiF, MgO, NaBr, NaF, NiO, PrBi, PuC, RbF, ScN, SrO, TbTe, UC, YN, YbO, ZrO.



CsCl: Fewer halides, very few oxides and chalcogenides. Note 8-8 coordination. CsCl itself has $a = 4.11$ Å. Other examples are CsBr, CsI, RbCl, AlCo, AgZn, BeCu, MgCe, RuAl, SrTl.



ZnS (zinc blende): ZnS is also found in the wurtzite structure. In cubic (blende) ZnS, the cell parameter is 6.23 Å. Note the 4-4 coordination, and the relation to the diamond crystal structure. Other examples are AgI, AlAs, AlP, AlSb, BAs, BN, BP, BeS, BeSe, BeTe, CdS, CuBr, CuCl, CuF, CuI, GaAs, GaP, GaSb, HgS, HgSe, HgTe, INAs, InP, MnS, MnSe, SiC, ZnSe, ZnTe.



Radius ratio recap

The *Radius ratio* rule states that a coordination polyhedron is formed around each cation. The distance between the cation and the anion is the sum of the ionic radii ($r_A + r_C$). The number (coordination number CN) of anions around the cation is determined by the radius ratio r_A/r_C. Also see the in-class handout.

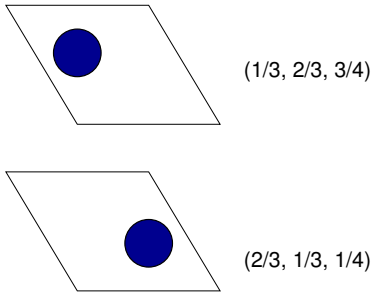
The crystal systems

See the in-class handout.

Some hexagonal structures

hcp – the structure of Mg The cell parameters are $a = 3.20$ Åand $c = 5.20$ Å.

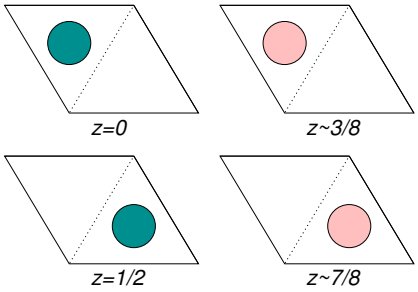
The cell comprises one Mg atoms at (2/3,1/3,1/4) and the other at (1/3,2/3,3/4).



Graphite The cell is $a = 2.4612$ Åand $c = 6.7090$ Å. The atoms are at (0,0,1/4), (0,0,3/4), (1/3,2/3,3/4) and (2/3,1/3,1/4).

Wurtzite, the other ZnS structure $a = 3.81$ Å $= 6.23$ Å

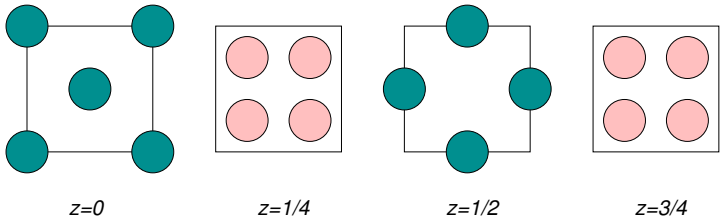
Atom	x	y	z
Zn	2/3	1/3	0
Zn	1/3	2/3	1/2
S	2/3	1/3	∼3/8
S	1/3	2/3	∼7/8



More complex cubic structures

Fluorite CaF_2 fcc $a = 5.45$ Å

Atom	x	y	z
Ca	0	0	0
F	1/4	1/4	1/4

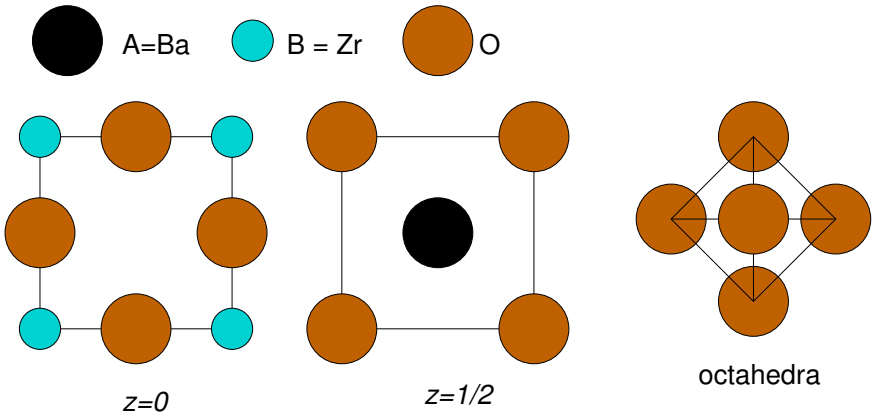


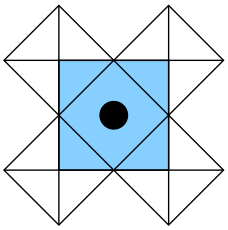
This structure type is also adopted by SrF_2, BaF_2, UO_2, ThO_2, Na_2O (the anti-type), ZrO_2 at high temperatures ...

ZrO_2 can be stabilized in the fluorite structure through doping with Ca^{2+} or Y^{3+} – these are *stabilized* zirconias and have many structural and electrochemical applications.

Perovskite ABO_3 $BaZrO_3$ (A = Ba, B = Zr):
Simple Cubic $a = 4.194$ Å

Atom	x	y	z
Ba	1/2	1/2	1/2
Zr	0	0	0
O	1/2	0	0





Miller indices

See the in-class handout.