Week 5

H. Finishing Close Packed Structures

NaCl Structure type

Exercise: What type of array does the NaCl structure type have? F-centered array
Is it close-packed? ccp

Which and what how are the layers stacked? ABC…
Along what direction can you see the layers? Body diagonal or 3-fold rotational axis.

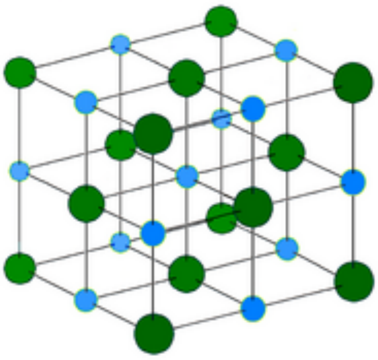
And how would you describe it? Ccp anion array with the octahedral holes filled by cations.

What about the tetrahedral holes? empty

The structure can be described also as $NaCl_6$ or $ClNa_6$ octehedra that share common edges. CN=6 and the ratio of anions to cations is 1:1.

Green sphere = oxygen; blue sphere = metal
Space group Fm3m (cubic)
Lattice parameter a ~ 5.64 Å; Z = 4

Atom	Site	x	y	z
O	4a	0	0	0
M	4b	½	0	0



What materials have NaCl Structure?

A huge number of AB (binary structures) have the rocksalt structure. The structure is formed by most monoxides of the first transition series, except CuO and ZnO, adopt the rocksalt structure. Further, halides and hydrides of alkali metals and Ag^+ as do a large number of chalcogenides of divalent metals (group 16 elements) typically including sulfides, selenides, tellurides.

Defects:

Sodium Chloride structures are prone to have point defects. There are two major types of defects stoichiometric and nonstoichimetric, the only difference is in stoichiometric defects, what you see with NaCl structure is that the chemical composition is unchanged with the defect that occurs.

3 common defects:

1. Schottky defect: where there is a cation and anion vacancy. So, it is essentially a point defect. Because the defects have an effective charge and the charge is opposite, they tend to associate with one another and the energy associated with the dissociations of hole pairs is 120 kJ/mol. These are intrinsic to the system, meaning they naturally occur.

The number of defects, n_s, is dictated by temperature. The equation to determine this is

$$n_s = N_A \exp(-e_s/2RT)$$

$e_s =$ energy required to form such a defect, for NaCl it is 192 kJ/mol
N_A is avegadros number 6.022 $*10^{23}$
R is the gas constant = 8.31 J/Kmol
T is temperature in K

For NaCl, $e_s \sim 192$ kJ/mol

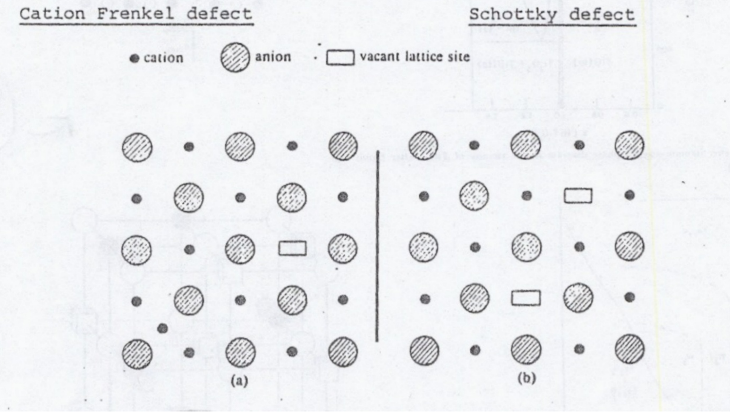
2. Frenkel defects: is a stoichiometric defect, where an atom is displaced from its original site and lands in a hole that is normally empty so these result in interstitial vacancies.

AgCl, which has the NaCl structure. The silver goes from an octahedral site to an empty tetrahedral site. These are intrinsic to the system, meaning they naturally occur.

The site looks like the following in the structure, it is actually 8-coordinate with 4 silver and 4 chlorine. Likely there is some covalent interaction between silver ions which stabilizes this defect. For hard ions, like Na, you will not see this defect often because for cations that are purely ionic it is less likely to want to be surrounded by other Na ions.

These defects also tend to associate with one another. Often the defects are produced at high temperature so for materials prepared at high temperature they often have a larger number of defects than the thermodynamic equilibrium concentration. You have to cool very slowly to help this problems.

Can anyone think of a way to promote defects in materials? You can bombard for instance with high energy radiation.



3. Non-stoichiometric Interstitial vacancies: Are non-stoichiometric and occur for instance when you dope in a metal or a different oxidation state. It can be the same metal or a different one. The best example is FeO where the stoichiometric material exhibits Rock salt structure, but the non-stoichiometric material $Fe_{1-x}O$ has Fe^{3+} in tetrahedral holes. So you would have some Fe vacancies in the octahedral holes and the new higher oxidation state ion goes into tetrahedral holes. It is said that these types of defects often cluster together as in the previous cases, but these are of course extrinsic to the system. The new chemical formula would be $Fe^{2+}_{1-3x}Fe^{3+}_{2x}O$

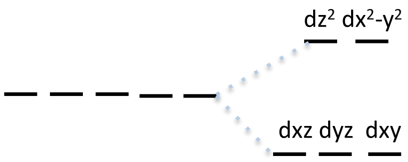
Why are these defects important?

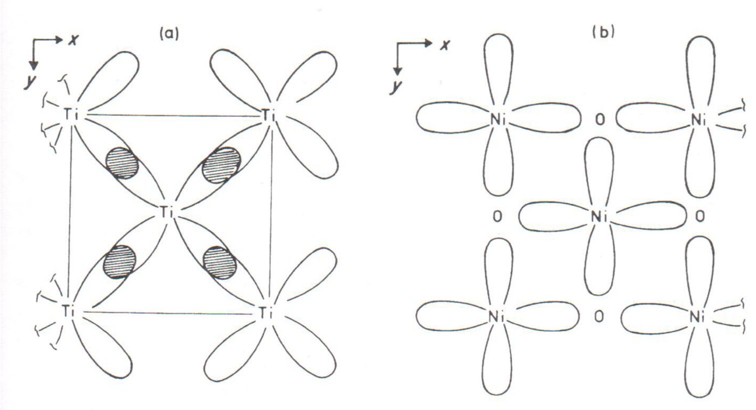
These holes are responsible for transport properties in oxides such as ionic diffusion, conductivity, and optical properties.

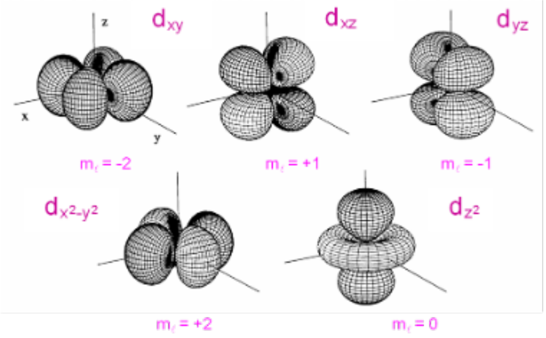
Exercise: Many early transition metal oxides, like TiO and VO, exhibit metallic level conductivity while late transition metal oxides, like NiO, do not. Can anyone guess why? Please consider crystal field theory.

Answer: In NaCl structure metal is in what coordination environment? Octahedral hole so this means that the orbitals which point along the ligand path are what?

Consider the Eg, dx2-y2 or dz2 orbitals point towards the oxygen in the rocksalt structure and the t2g orbitals point along the path of the other metals. So, if you look at the electron configuration of Ni2+, 3d8, the t2g orbitals are completely filled while the t2g of the Ti is 3d2 are partially filled. Metals with partially filled t2g orbitals that point towards other metals can have strong overlap allowing the formation of a band that provides metallic level conductivity, while metals having filled t2g orbitals do not.







I. Radius Ratio Rule

This rule is typically used for predominately ionic structures where you can predict the coordination numbers and the structures by taking electrostatic information into consideration. The key is that cations and anions surround themselves with as many oppositely charged entities as possible in order to maximize attractive interactions and hence also the lattice energy. You can predict the structures that form based on the size and charge of the ions.

Radius ratio is rc/ra (radius of cation over anion).

The minimum radius ratio that an ion can have in these different coordination environments is below.

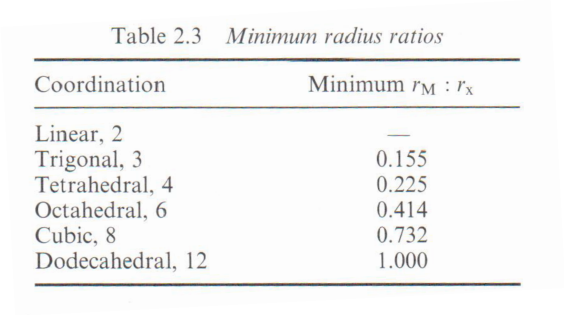


Table 2.3 *Minimum radius ratios*

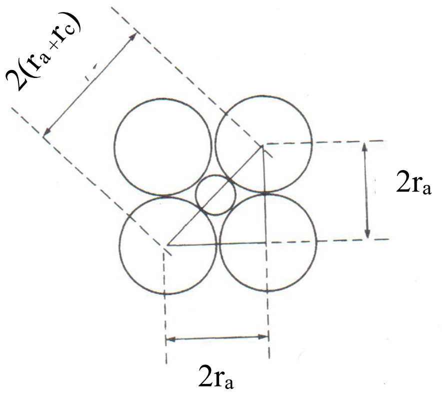
Coordination	Minimum $r_M : r_X$
Linear, 2	—
Trigonal, 3	0.155
Tetrahedral, 4	0.225
Octahedral, 6	0.414
Cubic, 8	0.732
Dodecahedral, 12	1.000

There are two rules to consider when calculating the radius ratio.

1). The cations must be in contact with the anion. This means that if a cation rattles around in the cage (tetrahedral or octahedral hole) then it decreases stability of the structure.

2). Neighboring anions may or may not be in contact. If we want to calculate the minimum radius ratio, we assume the anions are in contact.

Using these rules you can calculate the cation size that can be in an interstitial site. So lets calculate the minimum radius for a cation in an octahedral site. Consider the image below as the equatorial plane of an octahedral complex.



If we consider Pythagorean theorem we have the following:

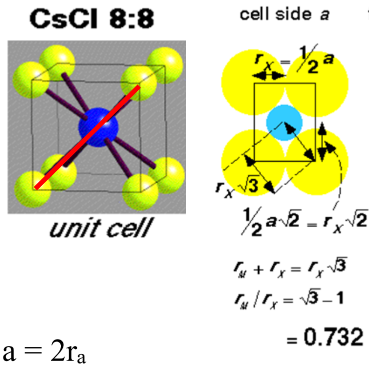
$4r_a^2 + 4r_a^2 = [2(r_a + r_c)]^2 \quad = \quad 8r_a^2 = [2(r_a + r_c)]^2$ then take square root of both sides

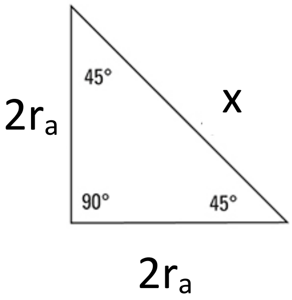
$2r_a\sqrt{2} = 2(r_a + r_c)$ so

$r_a\sqrt{2} = r_a + r_c \quad r_a$ so $\sqrt{2} - 1 = r_c/r_a = 0.414$

This means that the cation/anion ratio must be greater than or equal to 0.414. Below 0.414 the cation will rattle around in the cavity. Above 0.414, the anions will not touch. The cations can have a radius ratio up to 0.732 and then the cations become coordinated to 8 nearest neighbors. Please do the same calculation for the CsCl structure.

Exercise: I would like for you to do the same calculation but do it for CsCl structure.





$a = 2r_a$

so $(2r_a)^2 + (2r_a)^2 = x^2$

$4ra^2 + 4ra^2 = x^2$
$x = 2r_a\sqrt{2}$

solve now for the plane shown in yellow.
$8r_a^2 + 4r_a^2 = [2(r_c + r_a)]^2$

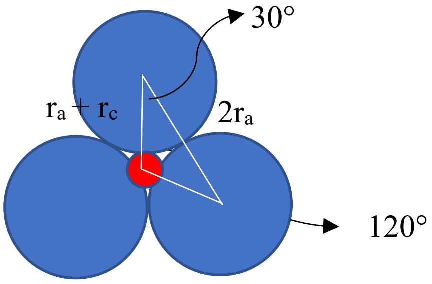
$2r_a\sqrt{3} = 2r_c + 2r_a$

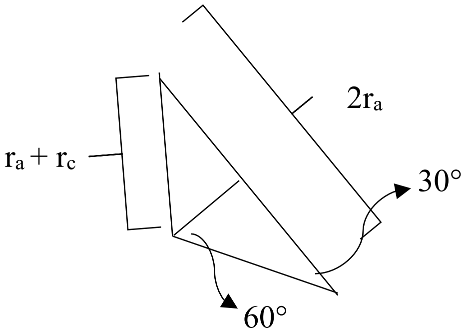
$r_a\sqrt{3} - ra = r_c$ so $\sqrt{3} - 1 = r_c/r_a = 0.732$

Answer: if r_c/r_a is smaller than 0.732 the cation rattles and the structure is unstable. If r_c/r_a is larger than 0.732 then the anions are moved apart.

Exercise: Try to calculate the minimum radius ratio now for a trigonal site.

So the following is a table to show the coordination number for for various Rc/Ra ratios.





$\text{Cos}(30) = r_a/(r_a+r_c)$
$0.8660r_a + 0.8660r_c = r_a$
$0.8660r_c = (1-0.8660)r_a$
$r_c/ r_a = 0.1547$

You should know that there are cases where things are borderline and so the radius ratio rule cannot always be strictly applied for instance if you look at GeO_2, the ratio of Ge/O is 0.43. This is slightly above the 0.414 limit that we described and it forms the SiO2 structure type, but it also readily transforms into a polymorph Rutile structure where the CN = 6.

Polymorph – has the same chemical composition but a different structure. This interconversion happens due to similarities in the lattice energies for the two structures. They can interconvert via temperature, pressure, or by simply coming into contact with the lower energy structure.

Discuss below with GeO_2, and HfO_2, and CeO_2.

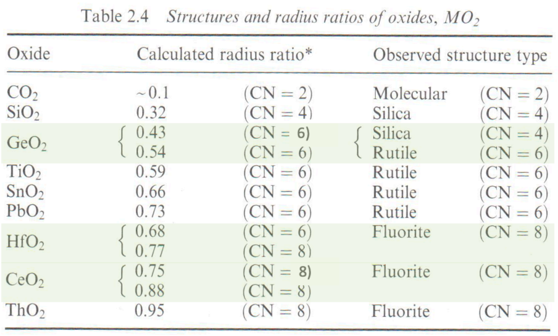
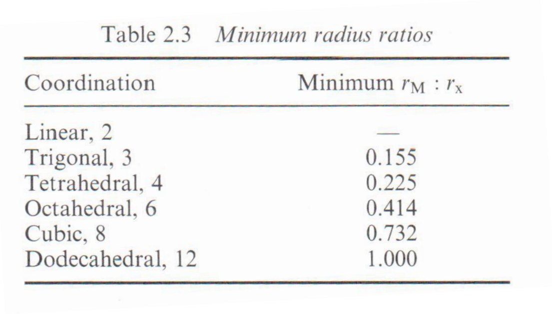


Table 2.4 *Structures and radius ratios of oxides, MO_2*

Oxide	Calculated radius ratio*		Observed structure type	
CO_2	~0.1	(CN = 2)	Molecular	(CN = 2)
SiO_2	0.32	(CN = 4)	Silica	(CN = 4)
GeO_2	0.43	(CN = 6)	Silica	(CN = 4)
	0.54	(CN = 6)	Rutile	(CN = 6)
TiO_2	0.59	(CN = 6)	Rutile	(CN = 6)
SnO_2	0.66	(CN = 6)	Rutile	(CN = 6)
PbO_2	0.73	(CN = 6)	Rutile	(CN = 6)
HfO_2	0.68	(CN = 6)	Fluorite	(CN = 8)
	0.77	(CN = 8)		
CeO_2	0.75	(CN = 8)	Fluorite	(CN = 8)
	0.88	(CN = 8)		
ThO_2	0.95	(CN = 8)	Fluorite	(CN = 8)



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Please note in the above table, if you look at the calculated radius ratio from the crystal structures in the table on the left and the predicted coordination number, it quite well matches the observed coordination environment. There are only two deviations seen in the table and those are on the cusp of the minimum radius ratio shown in the table in the right.

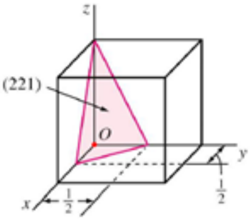
J. Lattice Planes, Miller Indices, and Indices of directions

Lattice planes are a concept that were introduced with braggs law of diffraction. A lattice plan is defined by the shape and dimensions of the unit cell. These lattice planes are used to define planes of atoms within a crystal structure. The planes of the atoms are separated by some distance referred to as d-spacing.

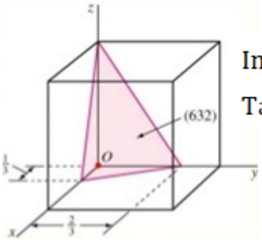
Lattice planes are defined by three numbers known as miller indices. To identify the Miller indices associated with the plane there are three steps

1). Identify the plane of atoms that you wish to obtain the miller indices for.
2). Find where the plane intersects the a, b, and c axes.
3). Take reciprocals of these intersection points.

So as an example, I give you a unit cell

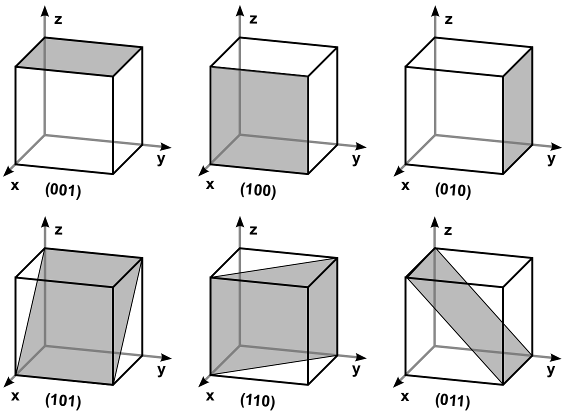


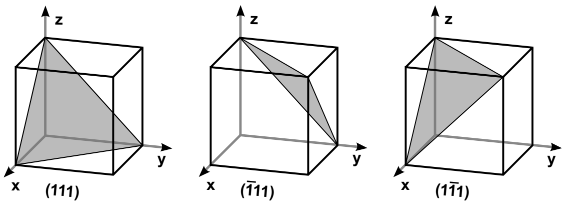
Intercept – (½, ½, 1)
Taking reciprocal (2 2 1)
Miller indices (2 2 1)



Intercept – (1/3, 2/3, 1)
Taking reciprocal (3 3/2 1)
Multiply by 2
Miller indices (6 3 2)

Exercise: Identify the miller indices:





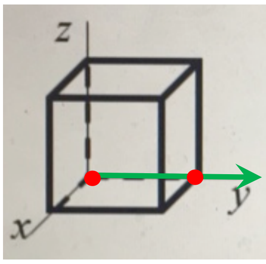
There are certain symbols used. For instance, {} is used to represent a set of planes.

{hkl} would include hkl, hlk, klh, khl, lkh, and lhk.
{100} = 100, 010, 001
() represents a single lattice plane

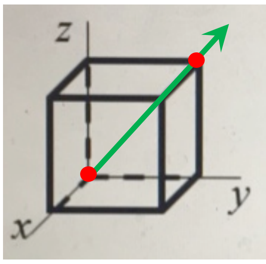
K. Miller indices of direction given by [uvw] indices are components of a vector not reciprocals as we discussed before.

1. Draw x,y, and z axes.
2. If there is a number larger than 1 divide by that number
3. Choose a point for the origin of your vector. This is where the vector starts. (if there is a negative number in the vector, move the origin in the positive direction along that axis.)
4. Start with your pencil on your chosen origin. Move your pencil u, v, and w directions. ·
5. Draw and label the endpoint.
6. Draw a line from your chosen origin to the point you just drew. Add an arrow head at the point.

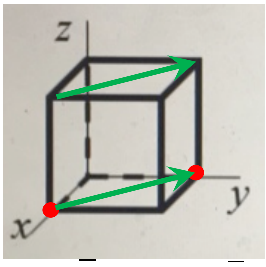
[010]



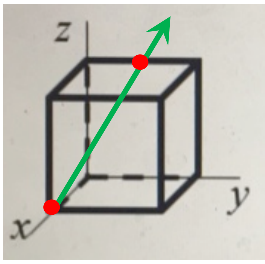
[011]



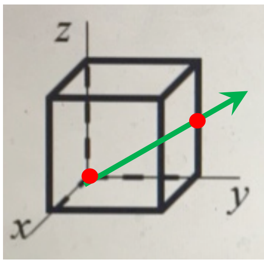
$[\bar{1}10]$ also equivalent to top one.



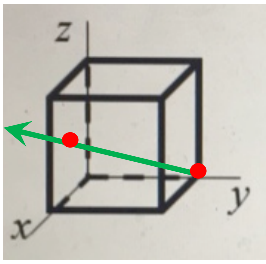
$[\bar{2}12]$ also $[\bar{1}$ ½ 1]



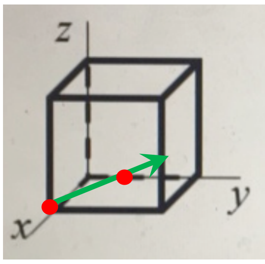
Exercise [021] also [0 1 ½]



$[1\bar{2}1]$ also [½ $\bar{1}$ ½]



$[\bar{2}10]$ also $[\bar{1}$ ½ 0]



<> represents a direction, this direction is orthogonal to the lattice plane and represents and identical set of planes. So <100> is equivalent to [100], [001], and [010] also the negative ones [100], $[00\bar{1}]$, and $[0\bar{1}0]$

It is noted that for cubic systems the direction is always perpendicular to the plane that the same set of numbers identify, but for non-cubic systems this is not always true.