MME 2011
Ceramic Materials I

Midterm 1: %25 (%5 of the grade will come from the lab reports)

Midterm 2: %25 (%5 of the grade will come from the lab reports)

Final : %50 (%10 of the grade will come from the lab reports)

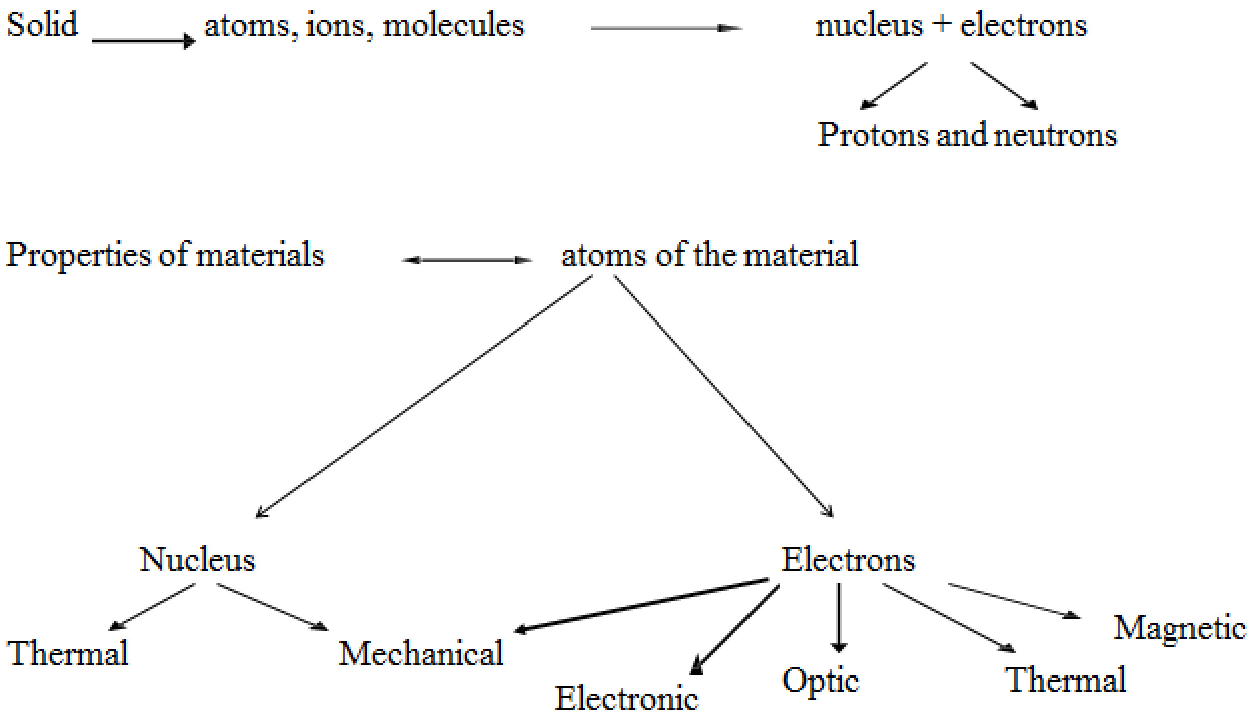
Textbook: D. Kingery, Bowen, Uhlmann, ***Introduction to Ceramics***, John Wiley Publ., 1960

Important Note 1 : 1st lab week topic will be " how to write a lab report?". You will write a number of lab reports during this course and this lecture is essential for you. Improper lab reports will not be graded during the course.

Important Note 2 : 2nd lab week "Lab Safety Rules and Instructions" will be explained. This lecture/training is obligatory. **You will not be allowed to pass this course, if you will not attend this training. There will be no make up for this training.**

Building Blocks of Materials

A brief review of the building block of materials:



Solid → atoms, ions, molecules → nucleus + electrons

Protons and neutrons

Properties of materials ↔ atoms of the material

Nucleus

Thermal

Mechanical

Electrons

Electronic

Optic

Thermal

Magnetic

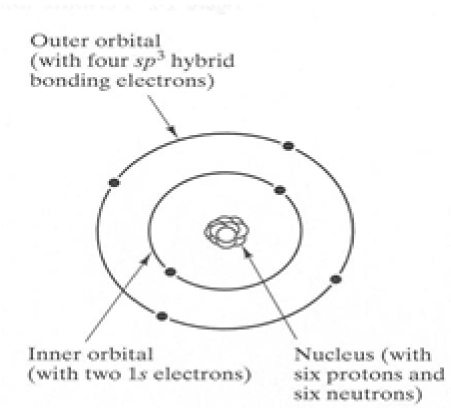


Figure 2-1 *Schematic of the planetary model of a* ^{12}C *atom.*

Nucleus → most of the weight → $1.66\ 10^{-24}$ gr

But a small portion of the space → $1.3\ 10^{-6}$ nm

Electrons → almost no weight → $0.911\ 10^{-27}$ g

→ But occupy > 99% of the volume 0.059 nm

→ Influence most of the properties

Duality in e^-'s nature → particle/wave characteristics

De Broglie: $\lambda = h/p$

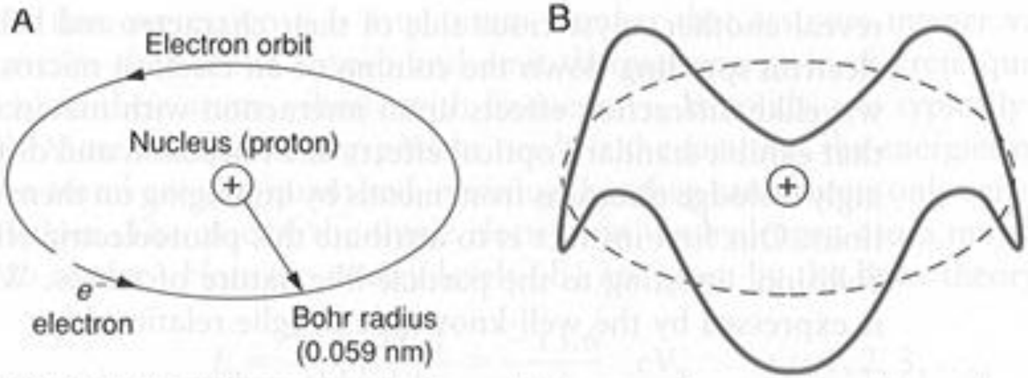
h - Planck's const.
λ - wavelength

$p = mv$

p – momentum
m – mass
v – velocity

electrons around nucleus

like standing waves in a vibrating string
they are constrained



(A) Model of a hydrogen atom showing an electron executing a circular orbit around a proton. (B) De Broglie standing waves in a hydrogen atom for an electron orbit corresponding to $n = 4$.

in 1-D

$$(d^2\Psi/dx^2) + (8\pi^2 m/4\pi^2\hbar^2)(E-V)\Psi = 0$$

E – total energy
V – potential energy

Solutions => Ψ only for discrete set of energy states

There is a simple relationship exists between

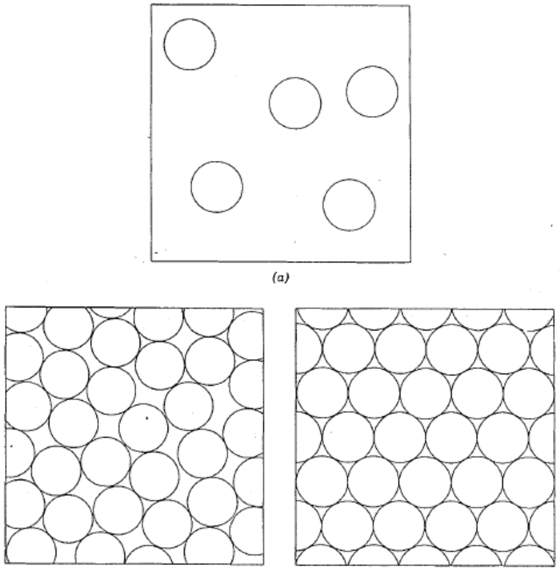
chemical properties of atoms ⟺ their electronic structure

usually, as Z increases, filling up of the shells with increasing quantum numbers BUT exceptions do exists

iron would have been $1s^22s^22p^63s^23p^63d^8$ but in reality
$1s^22s^22p^63s^23p^63d^64s^2$ (half-filled d shells!!!!! → Magnetic properties)

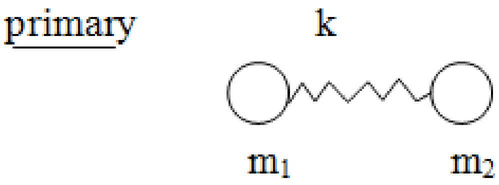
the discrepancies/inconsistencies are better explained with quantum mechanics approach

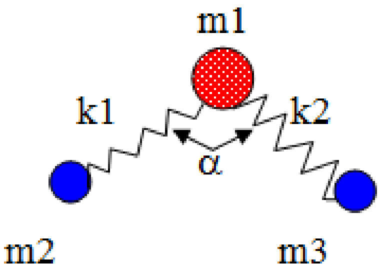
Let's simplify the shape of atoms as *solid spheres* to think easier and simpler

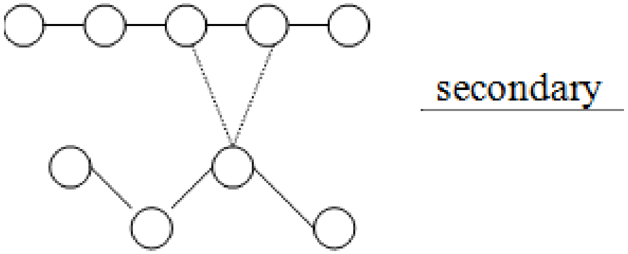

(a)
(b) (c)

Structures of (*a*) gas with widely separated molecules, (*b*) liquid with no long-range order, and (*c*) crystal with atoms or molecules having an ordered pattern.

Atomic Bonding







Primary bonds: Ionic, covalent, and metallic

→ Usually strong, stiff bonds
High moduli, usually high melting point

Secondary bonds: Van der Waals and hydrogen bonds

→ Usually weaker

IONIC BOND

Between strongly electropositive (metals) and strongly electronegative (nonmetals) elements

Electropositive => gives away electron(s) => becomes a positively charged
Ion ➔ a cation

Electronegative => takes up electron(s) ➔ becomes negatively charged ion
➔ an anion

two opposing charges attack each other by electrostatic forces

both ions with filled "outer shells"

important property of the ionic bond:

electrostatic field of the electron clouds of the ions ➔ spherically symmetric

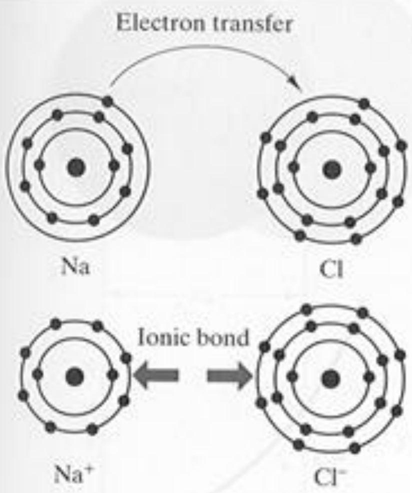


Figure 2-4 *Ionic bonding between sodium and chlorine atoms. Electron transfer from Na to Cl creates a cation (Na^+) and an anion (Cl^-). The ionic bond is due to the coulombic attraction between the ions of opposite charge.*

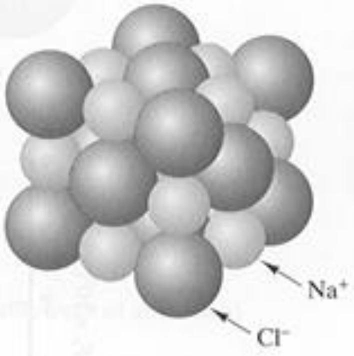


Figure 2-5 *Regular stacking of Na^+ and Cl^- ions in solid NaCl. This is indicative of the nondirectional nature of ionic bonding.*

➔ **NO** preferred directional character in the ionic bond

with the absence of directionality in the ionic bond

➔ atomic arrangement in ionic solids:

i) atoms (ions) arrange themselves to provide <u>local</u> **charge neutrality**

➔ alternating (+) and (-) **ions** in a symmetrical arrangement

ii) the packing fashion must be compatible with the different sizes of the ions.

Let’s see what happens when we bring an electropositive and an electronegative atom together

An example is Li and F

It takes about –5.4 eV to create Li+ from Li (i.e. to ionize the neutral Li atom)
And when the F atom grabs an electron it gives out 3.6 eV (also the fluorine atom is now ionized)

$$\mathrm{Li} + 5.4\ \mathrm{eV} \rightarrow \mathrm{Li}^+ + e^-$$
$$\mathrm{F} + e^- \rightarrow \mathrm{F}^- + 3.6\ \mathrm{eV}$$

And then we can gain energy as we bring F- and Li+ together from “infinity”

$$U = \int_{\equiv}^{ro} e^2/r^2\, dr \approx -e^2/r_o = -7.2\ \mathrm{eV}$$

$\mathrm{Li}^+ + \mathrm{F}^- \rightarrow \mathrm{LiF} + 7.2\ \mathrm{eV}$ (forming the molecule)

$\mathrm{Li} + \mathrm{F} + 1.8\ \mathrm{eV} \rightarrow \mathrm{Li}^+ + \mathrm{F}^-$ (ionization)

$$\mathrm{Li} + \mathrm{F} \rightarrow \mathrm{LiF} + 5.4\ \mathrm{eV}$$

By bringing Li and F together we lower the energy of the system and form a stable bond

As the (+) and (-) ions come together they do not collapse onto each other although there us an attractive force due to electrostatic attraction given by :

$$F = e^2 / (4\pi\varepsilon_0 r^2)$$

ε_0- permitivity of free space

$e^2 = |q^+| \, |q^-|$

r – interatomic separation

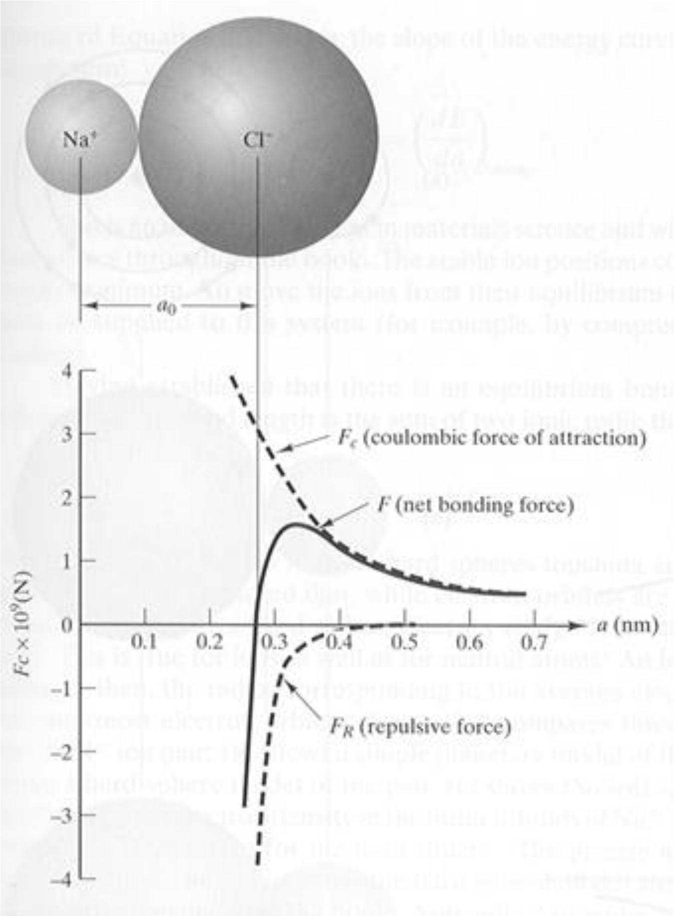


Figure 2-7 *Net bonding force curve for a $Na^+ - Cl^-$ pair showing an equilibrium bond length of $a_0 = 0.28$ nm.*

because as they come too close together the electron clouds start to overlap the work done to bring these ions together from infinity is the total force integrated over r

$$U = -\int_r^{\infty} F\,dr = -e^2/(4\pi\varepsilon_0 r)$$

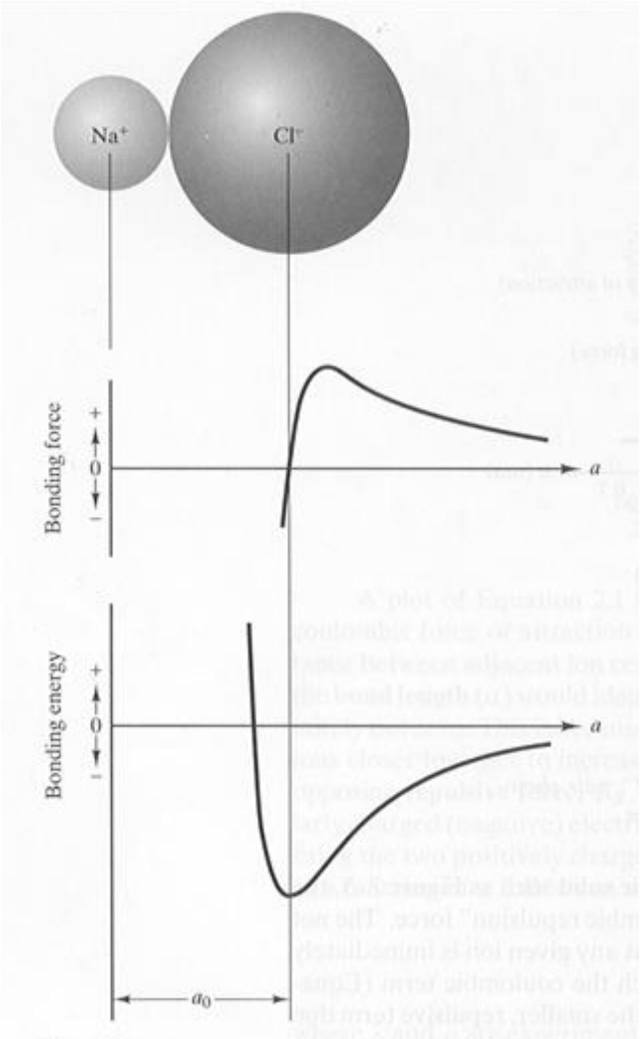


Figure 2-8 *Comparison of the bonding force curve and the bonding energy curve for a Na^+-Cl^- pair. Since $F = dE/da$, the equilibrium bond length (a_0) occurs where $F = 0$ and E is a minimum (see Equation 2.5).*

Why don’t collapse on to each other?

The overlap of the electron clouds from the two ions cause a very strong repulsion!!!

The total energy is given by contributions made by repulsive, attractive, and ionization forces…..

$$U_T = U_i - q^2/(4\pi\varepsilon_0 r) + B/r^m \qquad m \sim 10 \text{ for ionic bond}$$

The repulsive contribution starts becoming dominant @ small r!!

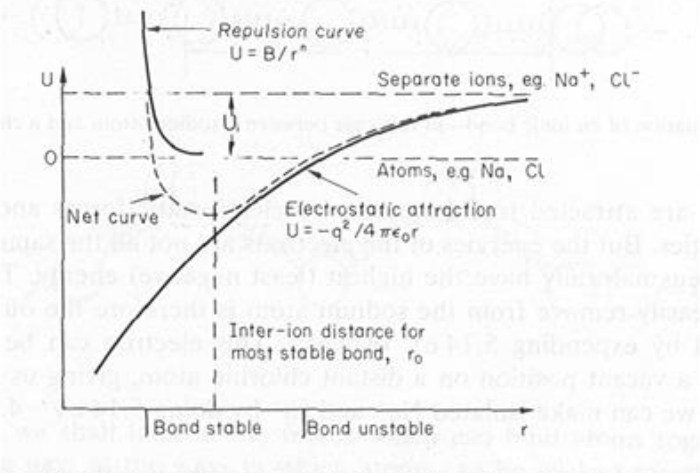


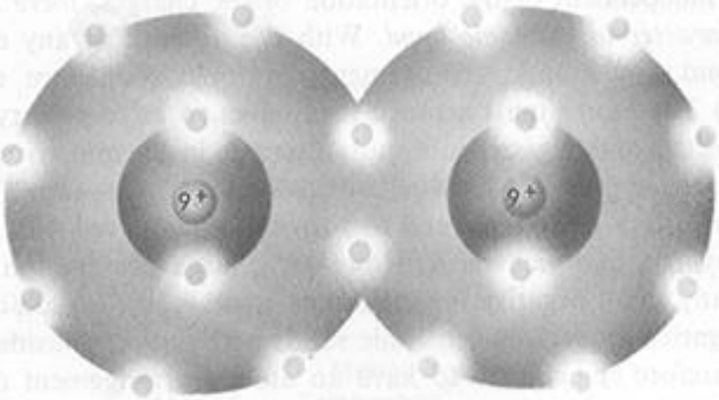
Fig. 4.4. *The formation of an ionic bond, viewed in terms of energy.*

Ionic bond is → strong
→ non-directional
→ exist mainly in ceramic materials and minerals
→ associated with high stiffness,
high melting point,
hard
brittle materials
poor electronic conductors
usually good thermal insulators
very good chemical resistance

COVALENT BOND

Forms by sharing outer **s** and **p** electrons,
mostly between atoms of elements near one another
in the periodic table

by sharing their electrons they both can have complete outer electron shells of elements near one another in the periodic table.



Covalent bonding in the F_2 molecule

By sharing their electrons they both can have complete outer electron shells.

Since the electrons are shared between the atoms forming the bond, covalent bond is extremely directional. In its purest forms it exists in diamond, silicon and germanium.

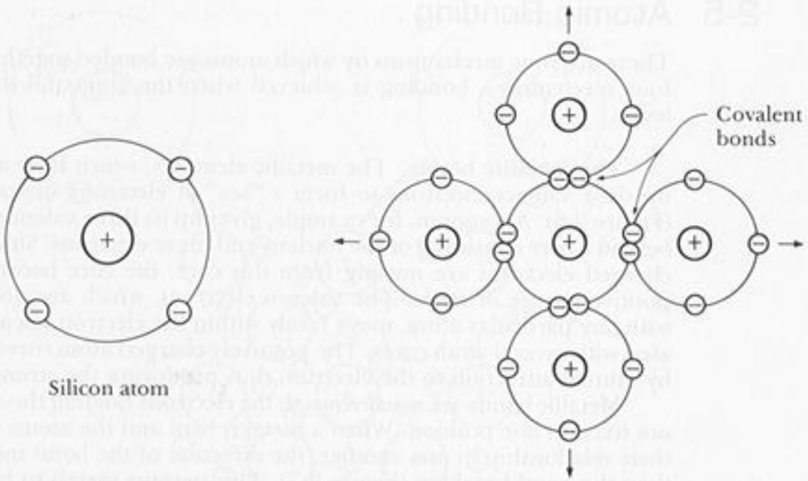


FIG. 2-9 Covalent bonding requires that electrons be shared between atoms in such a way that each atom has its outer *sp* orbital filled. In silicon, with a valence of four, four covalent bonds must be formed.

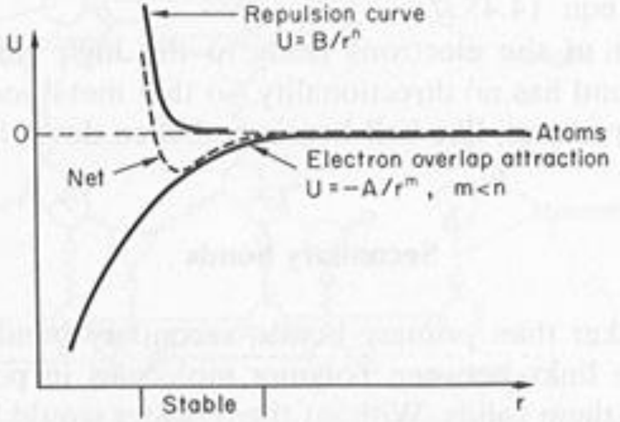


Fig. 4.6. The formation of a covalent bond, viewed in terms of energy.

Covalent bond is usually associated with large moduli,
E (high stiffness),
poor ductility,
poor electrical conductivity
very high T_m

many ceramics, polymers and even metals (high T_m, high E) are partly bonded with covalent bonds.

The total energy diagram for this type of bond is also similar to the ionic bond with the exponents being different

$$(U_T)_{\text{covalent}} = -A/r^m + B/r^n \qquad \text{where } m < n$$

strongly directional bonds with strong attractive and repulsive component in their total force curve ➔ very brittle materials.

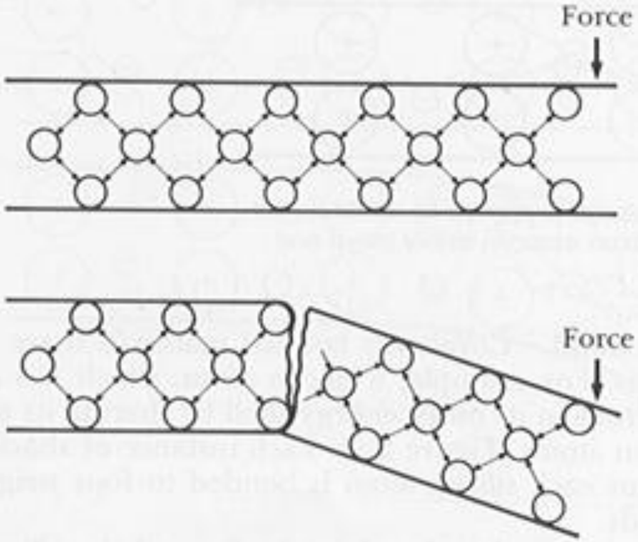


FIG. 2-11 When a force is applied to a covalently bonded material, the bonds may break. Covalently bonded materials are brittle.

METALLIC BOND

Forms mostly among atoms with only few electrons in their outer s and p orbitals ➔ mostly between metal atoms

Low valence metallic elements give up their valence electrons into the “soup” to form a “sea of electrons” surrounding the atomic cores;

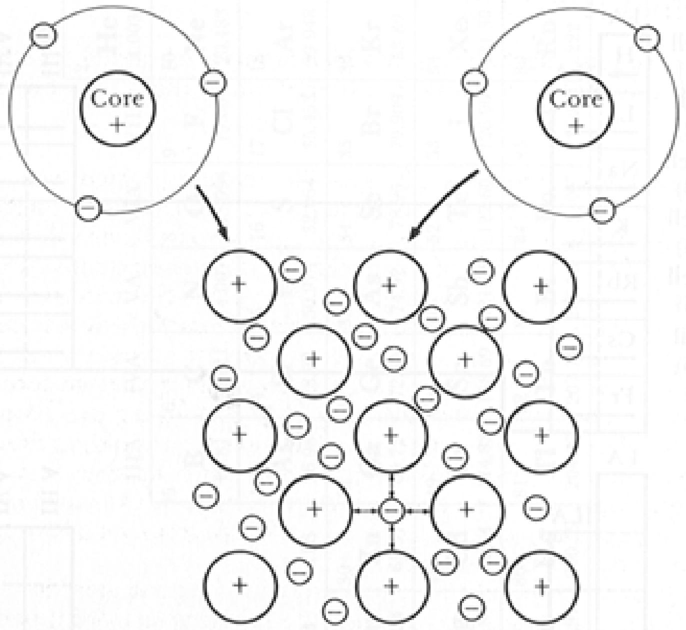


FIG. 2-6 The metallic bond forms when atoms give up their valence electrons, which then form an electron sea. The positively charged atom cores are bonded by mutual attraction to the negatively charged electrons.

once the valence electrons leave the atom, the core becomes effectively a positive ion. These (+) ions are held together by mutual attraction to the electrons between them.
Total potential energy of the metallic bond can be given by an equation similar to the one for covalent or ionic bond:

$$U_T = -A/r^m + B/r^n \qquad \text{with} \quad m < n$$

Metallic bond is somehow similar to ionic bond, but with ONE type of ionic core only
Metallic bond is non-directional, electrons are NOT fixed at one position thus, when a metal is bent, the atoms change their position to one another, and the direction of the bond is merely shifted

➔➔ metals have good ductility (easily deformable),
metals do NOT have strong primary directional bonds or any requirement for local charge neutrality → atoms slide over each other rather easily during deformation

since there is no directionality in the metallic bond ➔ metal ions tend to pack to give simple, highly dense structures, like ball bearings shaken down into a box.

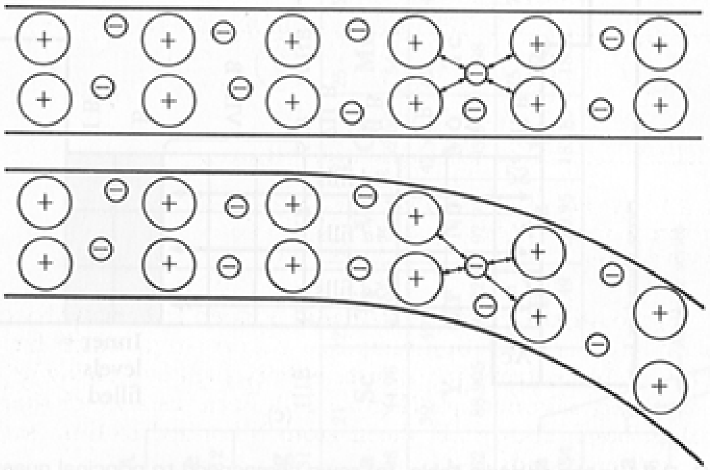


FIG. 2-7 Atoms joined by the metallic bond can shift their relative positions when the metal is deformed, permitting metals to have good ductility.

The free electrons in the metals are responsible for good electrical conductivity and high thermal conductivity:

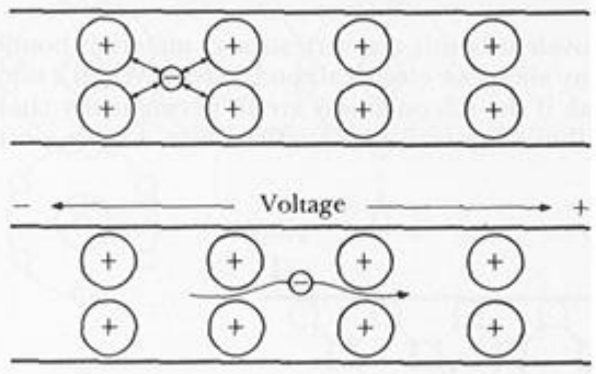


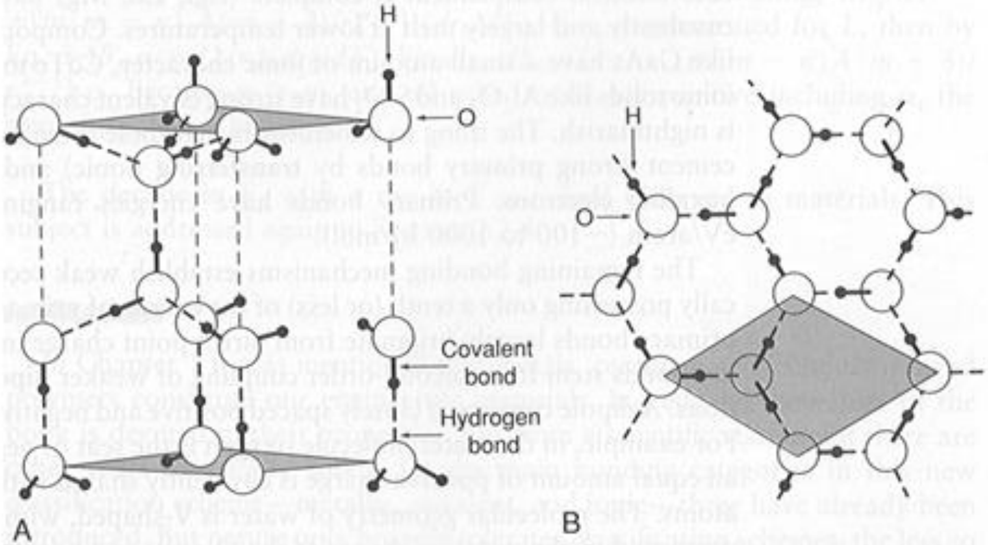
FIG. 2-8 When a voltage is applied to a metal, the electrons in the electron sea can easily move and carry a current.

Some metals with unfilled d or f orbitals do have covalent bonds which give them directionality in their properties and high melting points, T_m, like in Fe, W, Ti, Ta

SECONDARY BONDS

Van der Waals and hydrogen bonding

Typically 1/10 of the strength of primary bonds or less



Structure of ice shown in (A) side and (B) top views. (Also see Fig. 3-22D.) Intramolecular covalent bonds exist within the H_2O molecule. Intermolecular hydrogen bonds link H_2O molecules together. From K. M. Ralls, T. H. Courtney, and J. Wulff, *Introduction to Materials Science and Engineering*, Wiley, New York (1976).

They usually co-exist with the primary bonds in materials or between materials:

Van der Waals bonding: due to fluctuating **dipoles**

dipole – **dipole** interaction

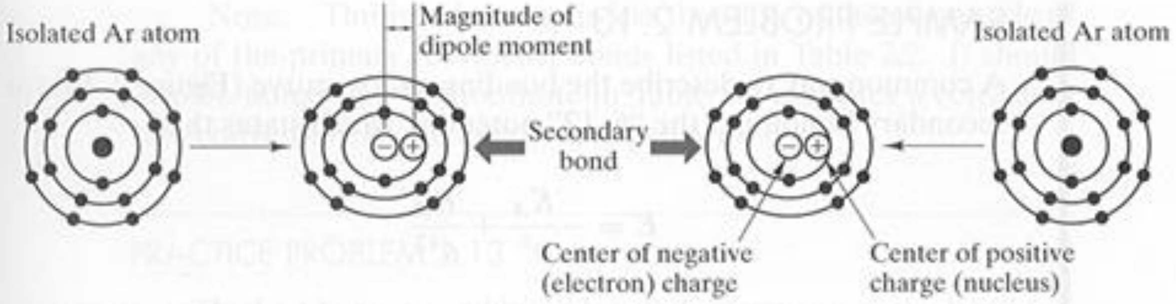
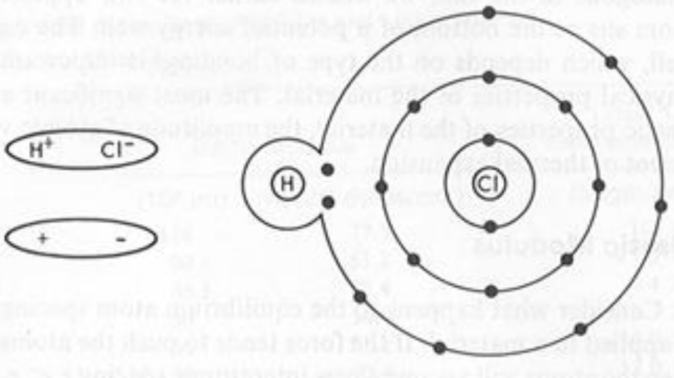


Figure 2-22 *Development of induced dipoles in adjacent argon atoms leading to a weak, secondary bond. The degree of charge distortion shown here is greatly exaggerated.*

Energy U_T for the van der Waals bond (usually around 0.1 eV):

$$U_T = -A/r^n + B/r^m \qquad n \cong 6$$



Dipole character of the HCl molecule

$m = 11\text{-}12$

generally weak bonds, somehow non-directional due to fluctuating character

Hydrogen Bond:

Hydrogen has only one e- → can only form one covalent bond with one anion, but then it is a mere cation (+) → it can act like a cation for another nearby anion → a weak attractive force is acting

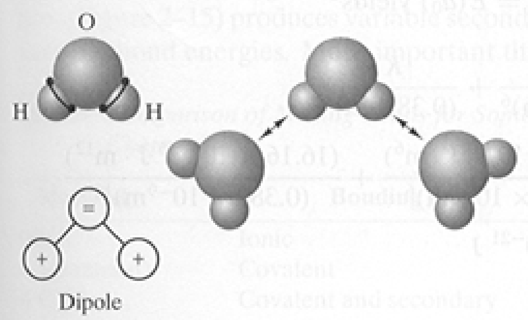


Figure 2-23 *"Hydrogen bridge." This secondary bond is formed between two permanent dipoles in adjacent water molecules. (From W. G. Moffatt, G. W. Pearsall, and J. Wulff,* The Structure and Properties of Materials, *Vol. 1: Structures, John Wiley & Sons, Inc., New York, 1964.)*

Hydrogen bonds are **also** operative between molecules containing permanent dipoles with hydrogen and strongly electronegative elements
Examples are HCl, HF

They are appreciably than primary bonds but are stronger than van der Waals bonds

Secondary bonds play a crucial role for life and aesthetic in coatings and paints

And other polymers and organic materials

Bonds and properties of materials:

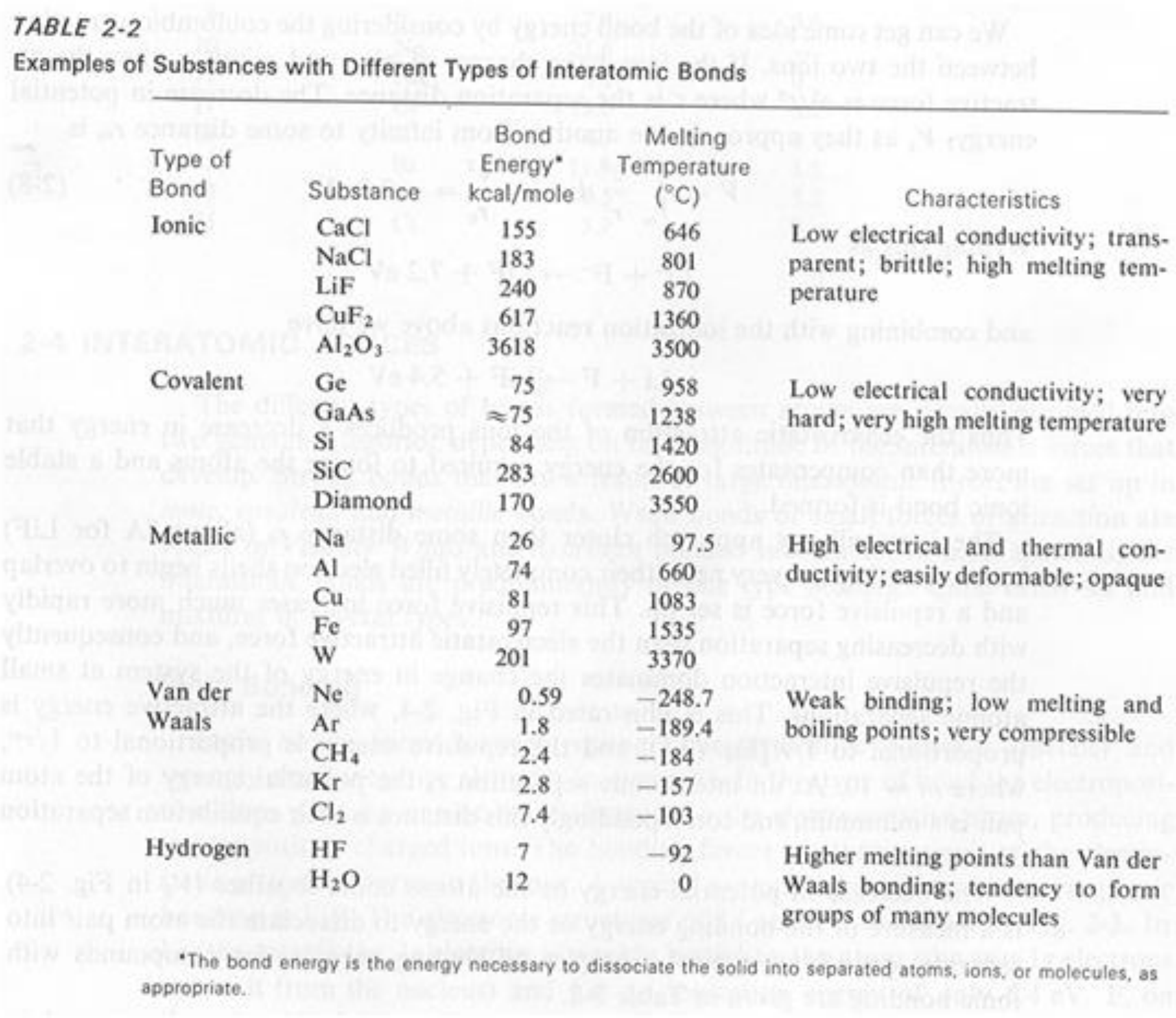


TABLE 2-2

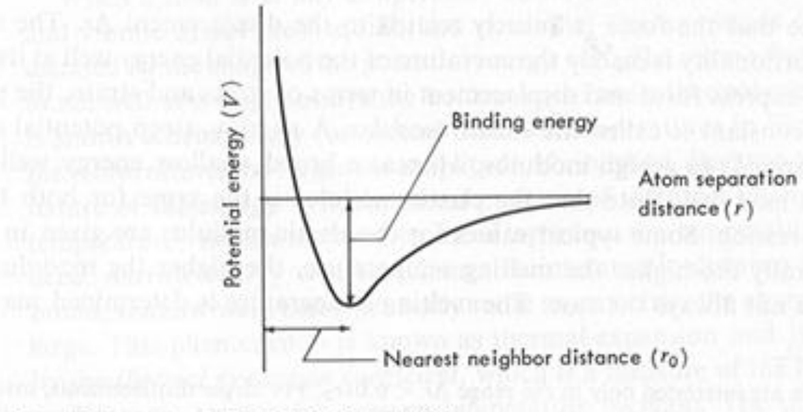
Examples of Substances with Different Types of Interatomic Bonds

Type of Bond	Substance	Bond Energy* kcal/mole	Melting Temperature (°C)	Characteristics
Ionic	CaCl	155	646	Low electrical conductivity; transparent; brittle; high melting temperature
	NaCl	183	801	
	LiF	240	870	
	CuF_2	617	1360	
	Al_2O_3	3618	3500	
Covalent	Ge	75	958	Low electrical conductivity; very hard; very high melting temperature
	GaAs	≈75	1238	
	Si	84	1420	
	SiC	283	2600	
	Diamond	170	3550	
Metallic	Na	26	97.5	High electrical and thermal conductivity; easily deformable; opaque
	Al	74	660	
	Cu	81	1083	
	Fe	97	1535	
	W	201	3370	
Van der Waals	Ne	0.59	−248.7	Weak binding; low melting and boiling points; very compressible
	Ar	1.8	−189.4	
	CH_4	2.4	−184	
	Kr	2.8	−157	
	Cl_2	7.4	−103	
Hydrogen	HF	7	−92	Higher melting points than Van der Waals bonding; tendency to form groups of many molecules
	H_2O	12	0	

*The bond energy is the energy necessary to dissociate the solid into separated atoms, ions, or molecules, as appropriate.

Binding Energy & Interatomic Spacing

Equilibrium nearest neighbour distance between two atoms (or ions) is where the energy of the system is at its minimum and there is no net force acting on the atoms (or ions).



Potential energy well for atoms in a solid

The shape of the energy well;
Depends on the type of bonding → determines several properties like;
stiffness (Young's Modulus)
coefficient of thermal expansion
melting point

ATOMIC ARRANGEMENT (in solids)

Depending partially on their bonding between them, atoms (ions) can be arranged in space with different degrees of **order**…..

In noble gases → complete lack of order (argon gas)

Bonds between the atoms in a molecule or directional bonds between nearest neighbor atoms will force a **short range order** between atoms like in a water molecule between oxygen and hydrogen atoms, or like in the silicon oxygen tetrahedra in **glass**

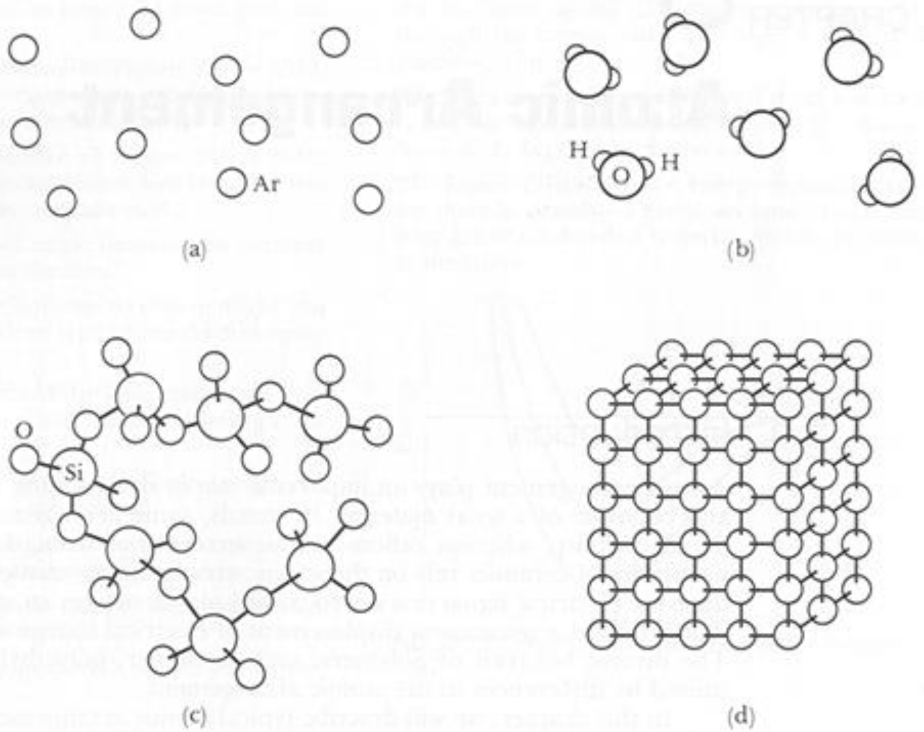


FIG. 3-1 The levels of atomic arrangement in materials. (a) Inert gases have no regular ordering of atoms. (b) and (c) Some materials, including steam and glass, have ordering only over a short distance. (d) Metals and many other solids have a regular ordering of atoms that extends throughout the material.

This short range order is typical of liquids or in the structure of so-called amorphous (amorph = lacking organization, or regular periodicity) materials.

The atomic arrangement in melts and amorphous solids are very similar. A major difference is their viscosities:

In amorphous solids the **disordered** structure is <u>frozen in</u>.

Crystalline solids exhibit "**long range order**" in the position and stacking sequence of atoms, molecules, or "**lattice points**"

In crystalline solids, each atom or molecule has <u>identical</u> surroundings in the crystal (except for the surface atoms)

Crystal Lattice Concept

Crystalline structure → consists of regular array of "points" in 3 dimensional space

With each of the **lattice points**,

there may be *none*, *one* or *more atoms* associated

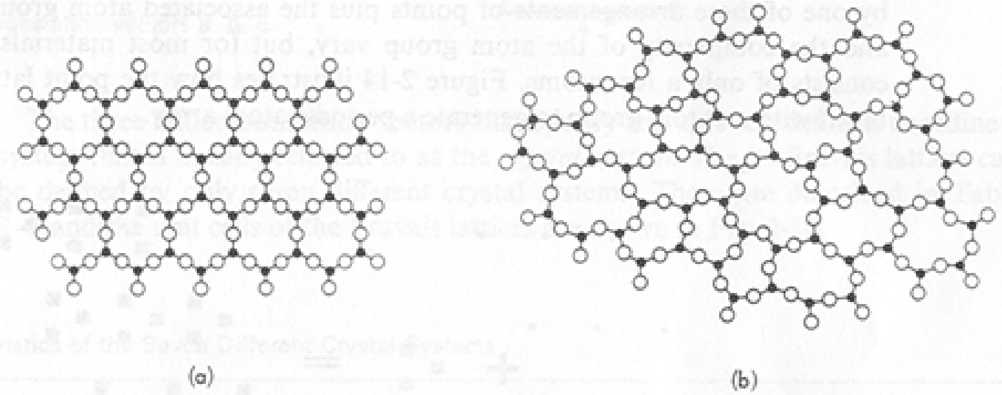
e.g. with each lattice point is one molecule of the above kind associated

Point lattice + atom group = periodic atom array

Schematic illustration of the generation of a periodic atom array using a point lattice and basic atom group

point lattice + atom group = periodic array of atoms

Crystalline and amorphous structures are built from exactly the same basic building blocks (short range order):


(a) (b)

Schematic illustration of (a) crystalline and (b) amorphous structure

how many ways to pack atoms in regular self repeating units???

Fortunately, there is only limited number of ways that one can pack lattice points in 3-D space such that each point has identical surroundings.
All the crystalline solids in the world can be described by these 14 ways of packing lattice points in space. (plus the local atoms group arrangement associated with each lattice point.)
Most of the time we have one or few atoms associated with one lattice point……BUT in a polymer this could be many atoms per lattice point!!!!!!!!!!!

The 14 different ways of packing ➔ 14 **BRAVAIS** lattices distributed to 6 (or 7) **crystal systems**.

Each **Bravais** lattice described by the smallest repeating unit:

UNIT CELL

Unit cell is defined by the three lattice translation vectors, $\vec{a}$, $\vec{b}$ and $\vec{c}$.
The magnitude of $\vec{a}$, $\vec{b}$ and $\vec{c}$ are called “lattice parameters”.

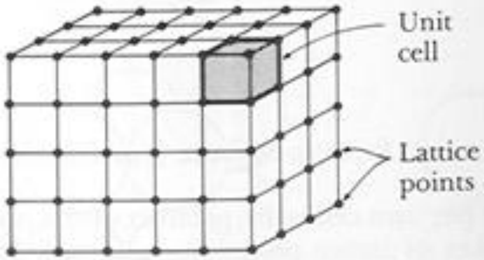
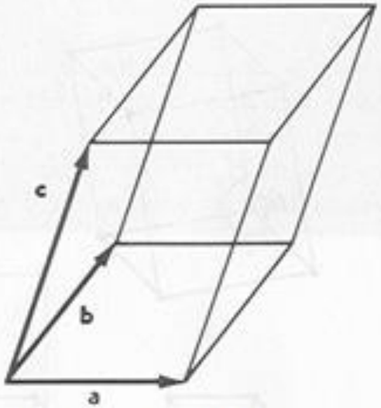
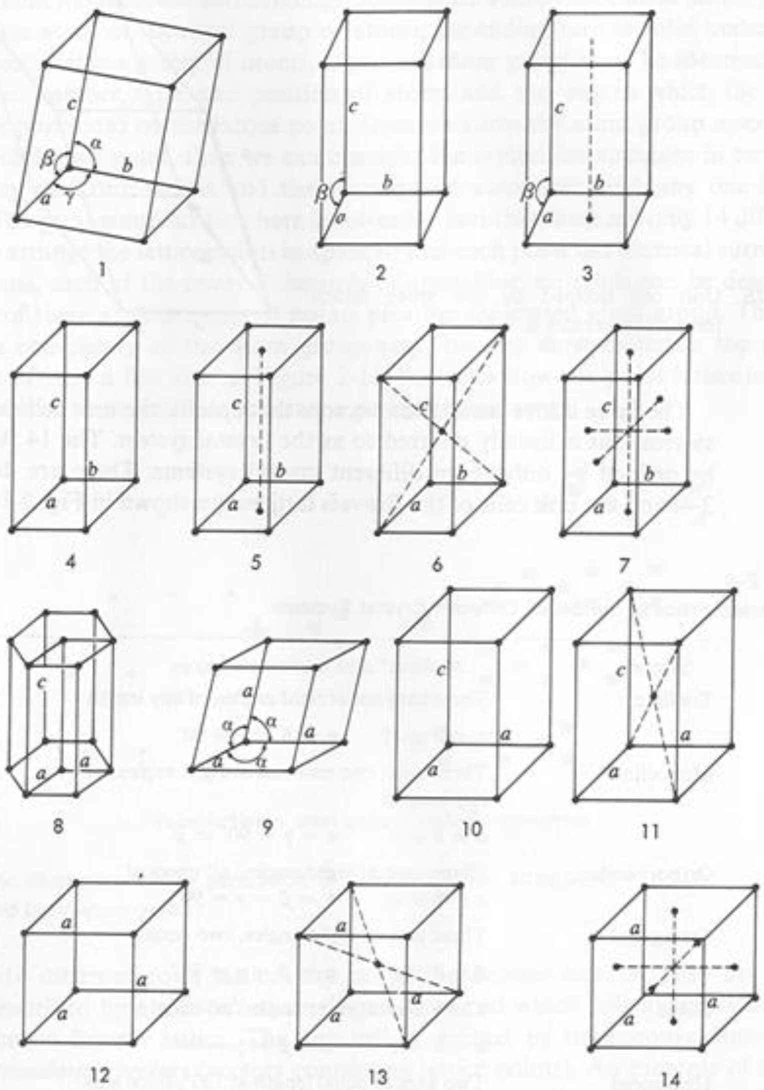


FIG. 3-2 A lattice is a periodic array of points that define space. The unit cell (heavy outline) is a subdivision of the lattice that still retains the characteristics of the lattice.

nit cell defined by the three lattice
ınslation vectors **a**, **b**, **c**



Depending on the ratio of a, b, and c and the angle between them, each unit cell is assigned to one of the 6 (or 7) crystal system.



6 The 14 point lattices illustrated by a unit cell of each: (1) triclinic, simple; (2) monoclinic, simple; (3) monoclinic, base centered; (4) orthorhombic, simple; (5) orthorhombic, base centered; (6) orthorhomic, body centered; (7) orthorhombic, face centered; (8) hexagonal; (9) rhombohedral; (10) tetragonal, simple; (11) tetragonal, body centered; (12) cubic, simple; (13) cubic, body centered; (14) cubic, face centered.

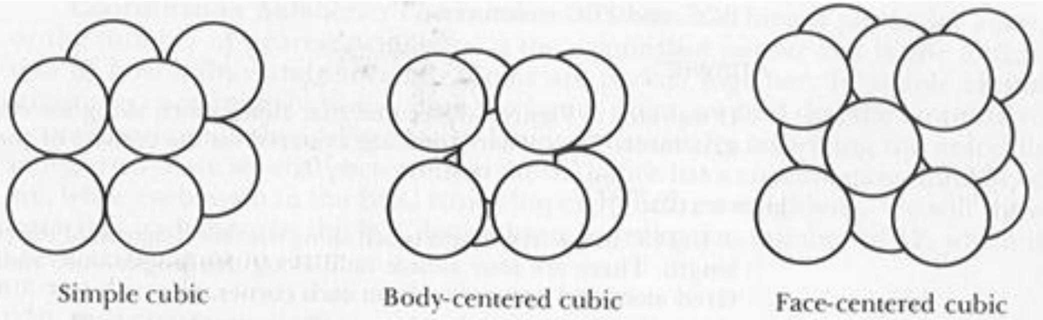


FIG. 3-5 The models for simple cubic (SC), body-centered cubic (BCC), and face-centered cubic (FCC) unit cells assuming only one atom per lattice point.

TABLE 2-4

The Characteristics of the Seven Different Crystal Systems

System	Axes[*] and Interaxial Angles	Examples
Triclinic	Three axes not at right angles, of any length $a \neq b \neq c$[†] $\alpha \neq \beta \neq \gamma \neq 90^\circ$	$B(OH)_3$, $K_2S_2O_8$, Al_2SiO_5, $NaAlSi_3O_8$
Monoclinic	Three axes, one pair not at right angles, of any lengths $a \neq b \neq c$ $\alpha = \gamma = 90^\circ \neq \beta$	$C_{18}H_{24}$, KNO_2, $K_2S_4O_6$, As_4S_4, $KClO_3$
Orthorhombic	Three axes at right angles, all unequal $a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	I, Ga, Fe_3C, FeS_2, $BaSO_4$
Tetragonal	Three axes at right angles, two equal $a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	In, TiO_2, $C_4H_{10}O_4$, KIO_4
Cubic	Three axes at right angles, all equal $a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	Cu, Ag, Ar, Si, Ni, NaCl, LiF
Hexagonal	Two axes of equal length at 120°, third axis at 90° to these $a = b \neq c$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	Zn, Cd, Mg, NiAs
Rhombohedral	Three axes equally inclined, not at right angles, all equal $a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$	Hg, Sb, Bi

[*] a, b, and c refer to the lattice parameters or dimensions of the unit cell.

[†] In this table ≠ means "not necessarily equal to, and generally different from."

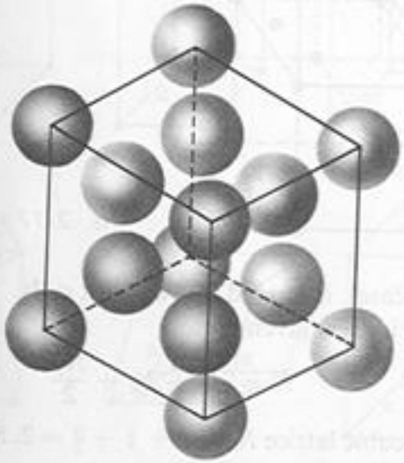


FIG. 2-19 The copper crystal structure (FCC Bravais lattice)

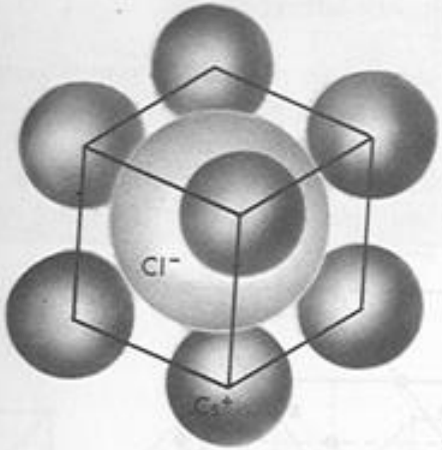


FIG. 2-18 Unit cell of CsCl

14 different ways of arranging atoms (ions), molecules in 3-D with long range order ➔ 14 Bravais Lattices

Lattice: periodic arrangement of points in 3-D sites of **identical** locations

Not all of these arrangements give the highest packing density of atoms (ions, molecules)

For example in metals:

FCC and HCP (hexagonal close packed) structures have the highest density of packing with 0.74

Metals with simple **metallic bond** → packed efficiently

Directional bonds → cause low packing density structures

(metals) theoretical (x-ray) density, ρ :

$$\rho = \left(\frac{\left(\frac{atoms}{cell}\right) \times (atomicmassofatom)}{(volumeofunitcell) \times (Avogadro's number)} \right)$$

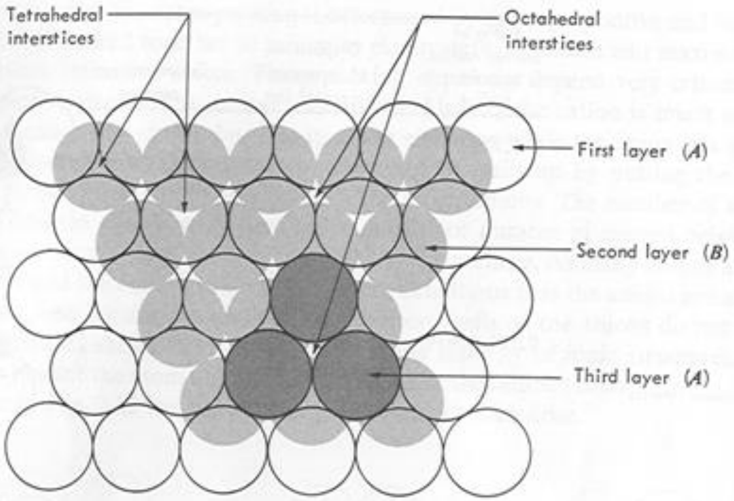
The two closed packed structures are very similar

The difference is in the sequence of stacking

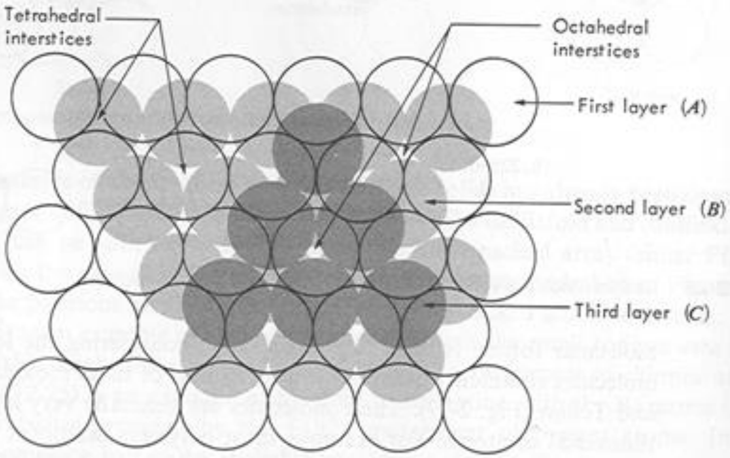
FCC: → A B C A B C A B C A B C

HCP: → A B A B A B A B A B

For spherical hard balls, both give highest solid packing ratio of 0.74

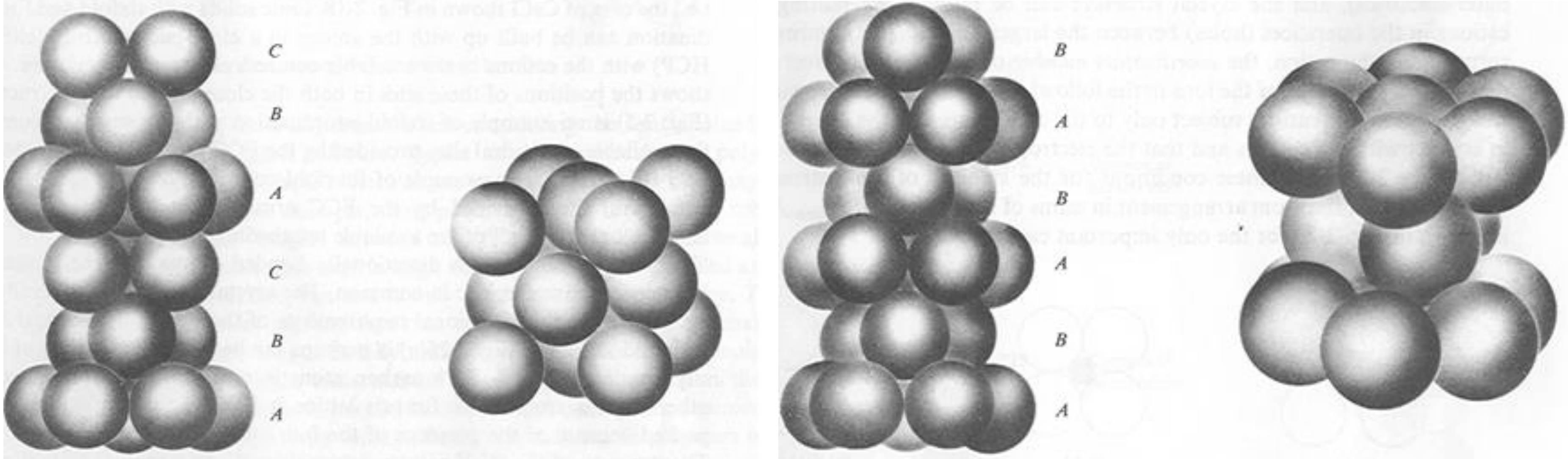


(a) HCP



(b) FCC

24 Octahedral and tetrahedral sites in HCP and FCC packing of atoms

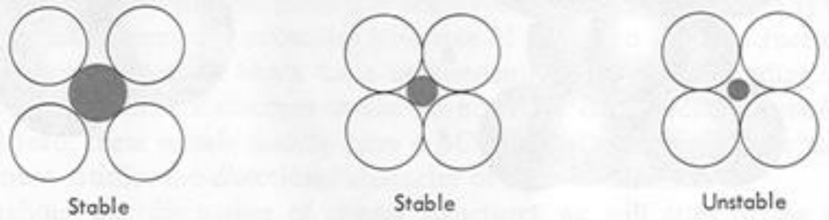


(b) Cubic close packing

(a) Hexagonal close packing

Packing sequence and unit cell for (a) HCP and (b) FCC structures

For identical balls packing ➔ touching balls (typical of metals)
But for ions of different sizes more varieties are possible →
Stable versus **unstable** packing for ionic materials

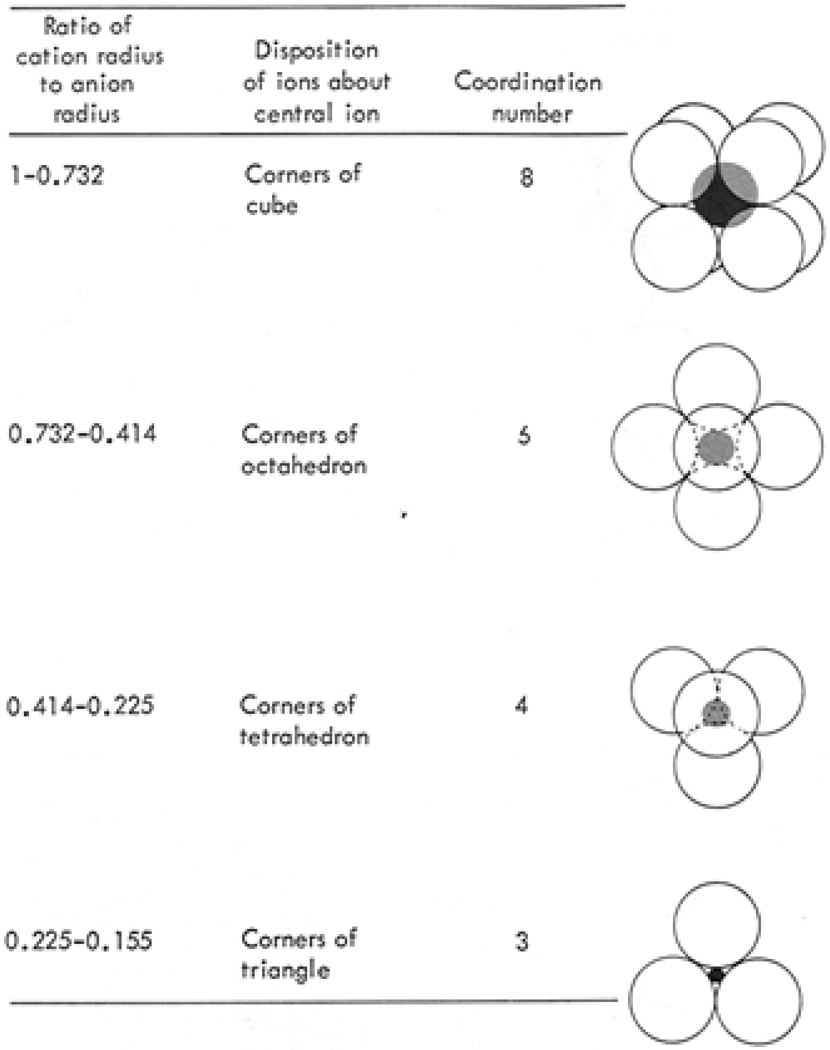


Stable and unstable ionic coordination configurations

Like charges will repel each other if they start to overlap.
Depending on the size ratio of the ions making up the material a certain coordination of a small ion with large ions around it is stable →

Some "<u>rules of thumb</u>" :

- as many anions as possible surrounding the cation
- anions always in contact with cations
- e^- -shells of anions do NOT overlap



Ratio of cation radius to anion radius	Disposition of ions about central ion	Coordination number
1-0.732	Corners of cube	8
0.732-0.414	Corners of octahedron	6
0.414-0.225	Corners of tetrahedron	4
0.225-0.155	Corners of triangle	3

Radius ratios for various atom arrangements in ionic bonding

CRYSTALLOGRAPHIC NOTATIONS

Points, directions, and planes in the unit cell.

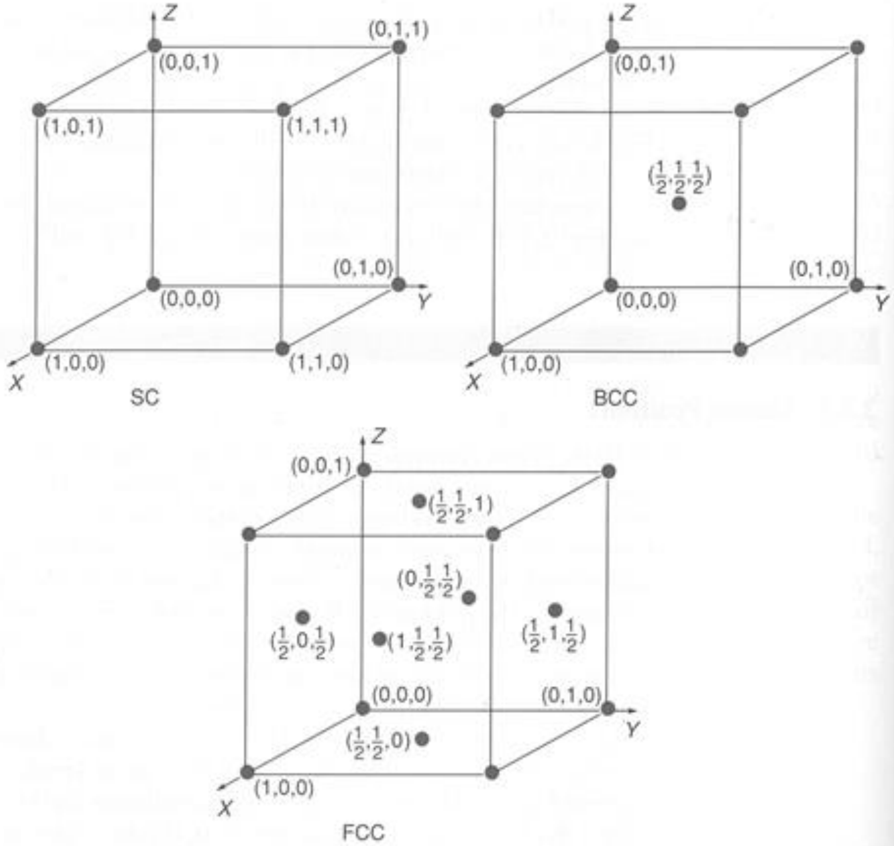
Unit Cell: the smallest, repeating, representative volume element of a crystal.

In order to locate certain points, atomic locations, directions or certain planes that atoms are arranged on, we have to agree on a system.

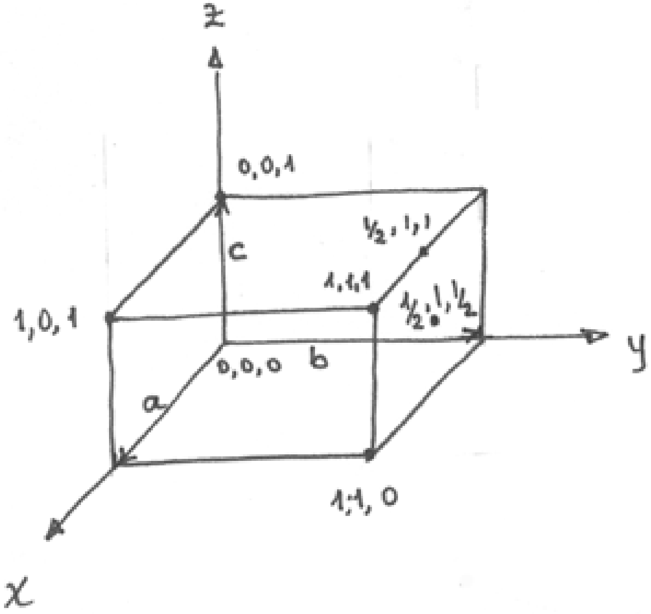
→ a right handed coordinate system that also reflects the properties of the crystal.

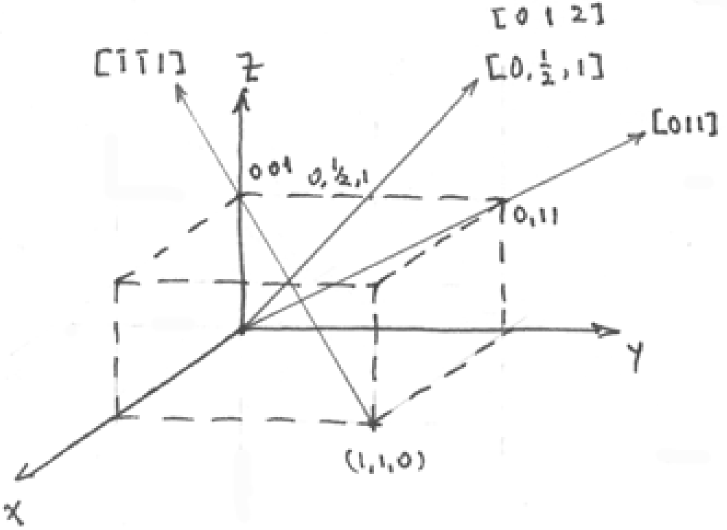
Unit lengths are the lattice parameters in each respective direction a, b, and c.

Then the directions are simply the vectors connecting the points in the unit cell.



Coordinate positions of points within SC, BCC, and FCC unit cells relative to the indicated origin of the x, y, and z axes.





→ A direction and its negative are not identical $[100] \neq [\bar{1}00]$

→ But a direction and its multiples are identical

$$[110] = [220] = [nn0]$$

→ Depending on the crystal system certain groups of directions may be equivalent. We refer to groups of equivalent directions as "<u>families of directions</u>"

As a figure of nomenclature, directions are designated with square brackets, i.e. [120], $[\bar{1}11]$, [12 1 1] etc.
A family of directions is designated by <110> brackets.

Directions in a family of directions are equivalent; like for example the edges of a cube [100]; [010]; [001]; $[\bar{1}00]$ etc. All are members of the family <100>

Crystallographic directions are indicated with square brackets and the **Miller indices** of directions are not separated with commas.
The negative of an index is indicated by a dash on top of the index, and read as "bar" e.g.

[101] = one o one

$[1\bar{1}1]$ = one bar one one

as a contrast to directions the positions in the unit cell are indicated with parenthesis and the Miller indices are separated by commas.

For cubic systems only;

Taking directions [uvw] and [u’v’w’] as vectors;

$\mathbf{D} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$ and $\mathbf{D}' = u'\mathbf{a} + v'\mathbf{b} + w'\mathbf{c}$

$\mathbf{D}\cdot\mathbf{D}' = |\mathbf{D}||\mathbf{D}'|\cos\delta$ or

$$\cos\delta = \frac{\boldsymbol{D}.\boldsymbol{D}'}{|\boldsymbol{D}||\boldsymbol{D}'|} = \frac{uu' + vv' + ww'}{\sqrt{u^2 + v^2 + w^2}\sqrt{u'^2 + v'^2 + w'^2}}$$

- The angle between two directions can be calculated

- The angle between two planes can be calculated

- The normal of a plane has the same indices with the indices of that plane!

Linear densities **and** ***planar densities*** **are extremely important for the following chapters!**

HOMEWORK

Read Chapter 1 (pages 1-20) of **Introduction to Ceramics, W.D Kingery**

Estimating bond type based on electronegativity (Pauling*)

Electronegativity:

- a measure of an atom's capacity to attract electrons
- sum of electron affinity (energy to add an electron) and ionization potential (energy to remove an electrons)

Compounds between atoms with a large difference in electronegativity are largely ionic (Fig 2.1). Compounds between atoms with similar electronegativity are mostly covalent (Fig 2.2).

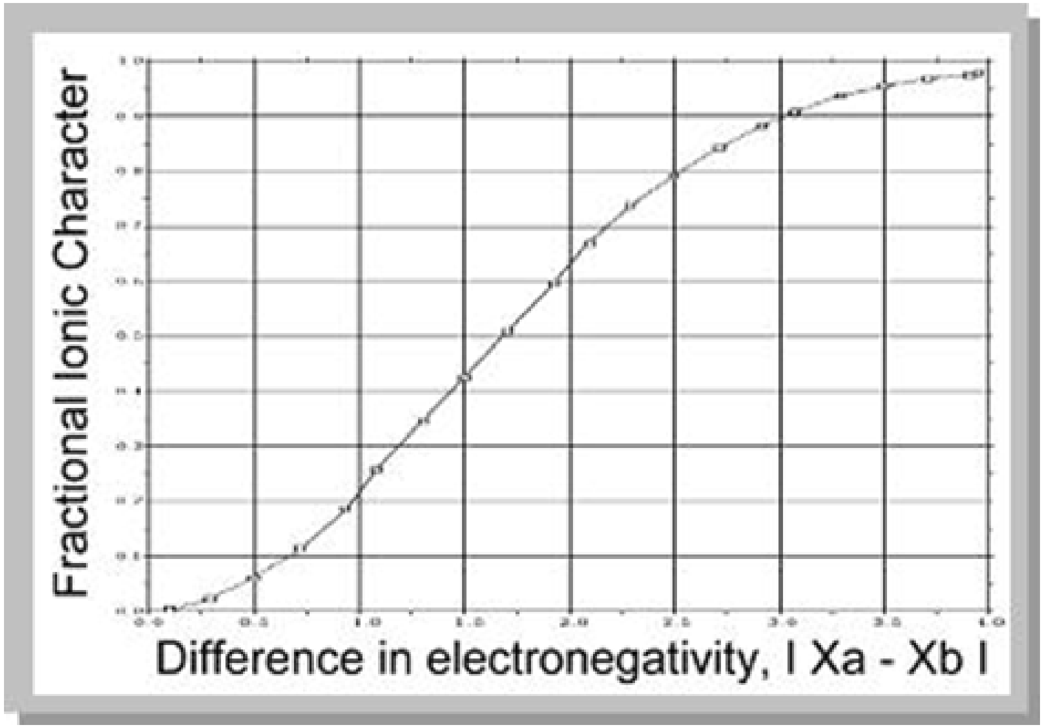


Figure 1.1Fraction of ionic character of bond A-B related to the difference in electronegativity Xa-Xb of the atoms.

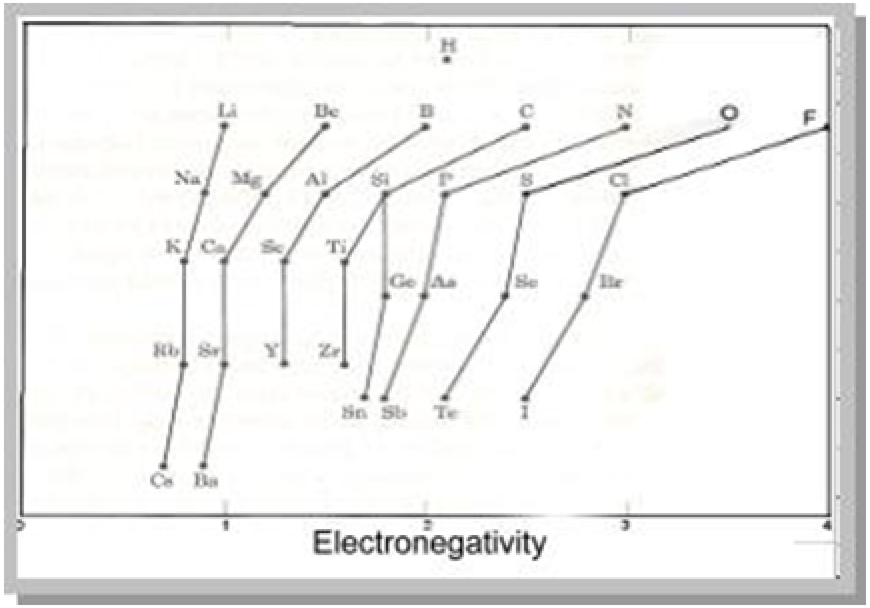


Figure 1.2 Electronegativity scale of the elements.

Ionic Crystals

Ionic Bonds (bonds between oppositely charged ions)

Energy, E_i, of the ionic bond is given by:

Attractive Coulombic Energy + Repulsive Orbital Overlap Energy + Ionization Energy.

$$\underbrace{\text{Attractive Coulombic Energy}}_{\mathbf{I}} + \underbrace{\text{Repulsive Orbital Overlap Energy}}_{\mathbf{II}} + \underbrace{\text{Ionization Energy}}_{\mathbf{III}}$$

As an example for KCl

$$E = \underset{\mathbf{I}}{-(e^2 / 4\pi\varepsilon_o R)} + \underset{\mathbf{II}}{(B/R^n)} + \underset{\mathbf{III}}{0{,}52\text{eV}}$$

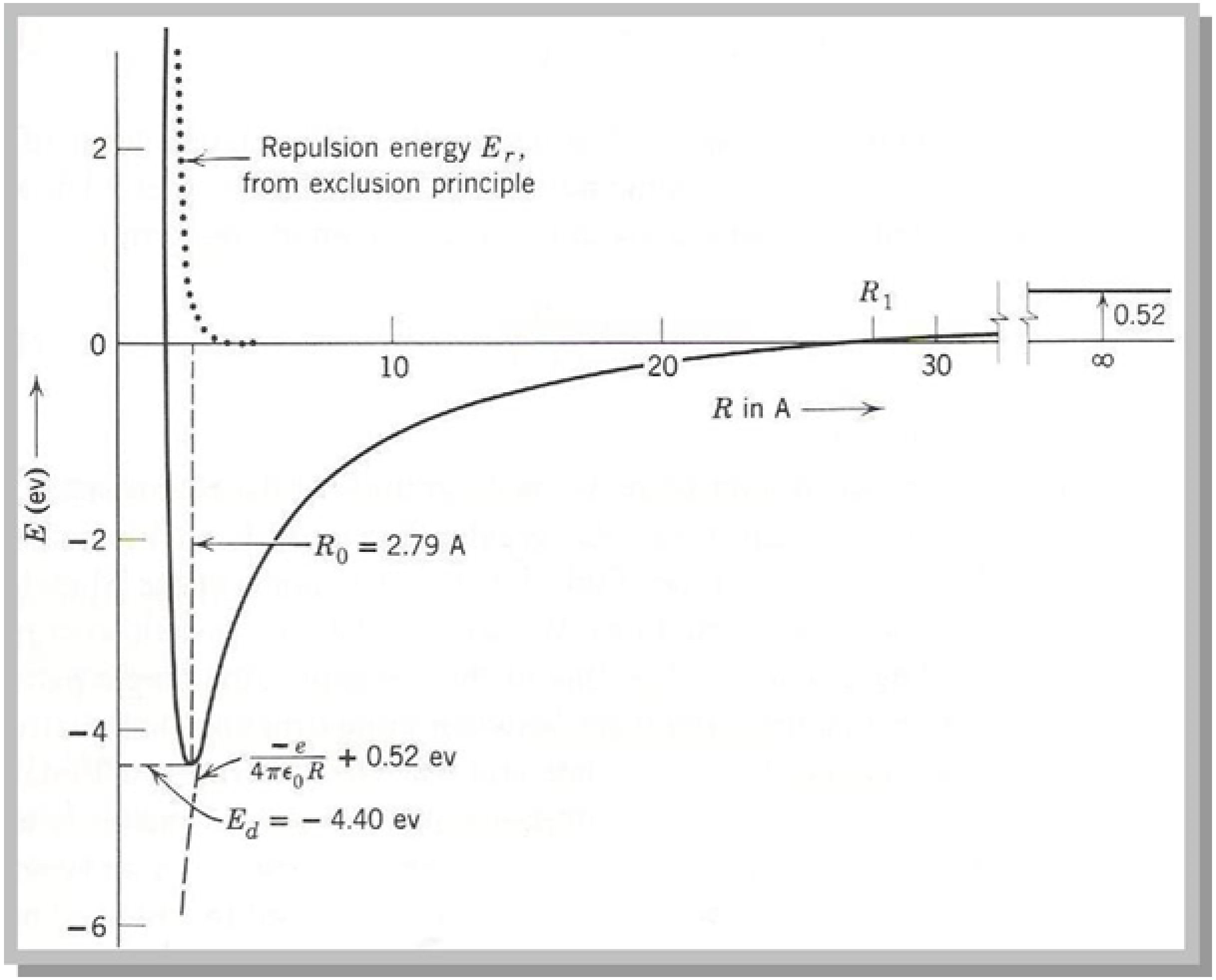


Figure 1.3 Contribution of electrostatic attraction and repulsion due to pauli exclusion to the ionic bond energy, where R is the ion seperation. The energy zero is referenced to neutral atoms. At infinite seperation, the energy is that for forming individual ions from neutral atoms. In this example for KCl, the ionization energy to form K^+ and the electon affinity for Cl^- together total +0,52eV.

Than in an ionic crystal one has to sum over all interaction between the ions in the crystal:

$$E_C = N\sum_j \left[\frac{Z_i Z_j e^2}{4\pi\varepsilon_0 R_{ij}} + \frac{B_{ij}}{R_{ij}^n} \right]$$ **(equation 2.1)**

Z_i and Z_j are the valences of the ions

$$E_C = N\left[\frac{Z_C Z_A e^2}{4\pi\varepsilon_0 R_0} \alpha + C \right]$$ **(equation 2.2)**

where **α = Madelung Constant, Z_A and Z_C are valences of anion and cation**

$$\alpha = -\sum_j \frac{(Z_i/|Z_i|)(Z_j/|Z_j|)}{X_{ij}}$$ **(equation 2.3)**

$$C = -\sum_j \frac{B_{ij}}{X_{ij}^n}$$

Physically, "Madelung constant" is the stability of crystal over the same number of isolated molecules (of say KCl). It is the coulomb energy (electrostatic energy) of an ion pair in a crystal relative to the coulomb energy of an isolated ion pair (strictly speaking only for MO type of compounds, for other stoichiometries, the values won't be exact).

$\alpha > 1$

C can be evaluated by the fact that, at equilibrium distance between ions, the net energy is minimum. In other words, repulsive and attractive forces are in balance. For a proof, we can differentiate E_{total} with respect to R, and set it to zero:

$$C = -\alpha\left[\frac{Z_C Z_A e^2}{4\pi\varepsilon_0} R_0^{n-1} \right]$$

then the whole binding energy equation becomes

$$E_C = N\left[\frac{Z_C Z_A e^2}{4\pi\varepsilon_0 R_0} \alpha * \left(n - \frac{1}{n} \right) \right]$$

Table 1.1Madelung Constants for common ionic structures

Structure Type	α
Rocksalt	1.748
Cesium Chloride	1.763
Zincblende	1.638
Wurtzite	1.641
Fluorite	2.519
Corundum	4.040

Ionic crystals usually have:

- Strong infrared absorption
- Transparency in the visible wavelengths
- Low electrical conductivity at low temperature
- High ionic conductivity at high temperature

Since electron distribution in ions is nearly spherical, the ionic bond is "nondirectional" in nature. Stable structures tend to be formed when an ion has maximum number of neighbours of opposite charge. That is usually when maximum packing density is obtained.

Madelung Constant is a measure of the stability of a crystal with a certain structure over isolated ion pairs. If the difference in energy between different types of the same stoichiometry is small, the material often has polymorphism. In other words, when two structures of the same compound have similar madelung constant; then, both structures can exist in nature. But which one is chosen? Can we predict it? Pauling's Rules can be used for this prediction.

Pauling Rules:

A set of 5 rules that allows us to understand how a certain ionic structure is chosen. It is based on the requirements that in any structure with ionic bonding character, a minimum energy is achieved when cation and anion attraction is maximized and like-ion repulsion is minimized. Thus,nearest neighbor coordination numbers are determined

Pauling's rules are obeyed; provided that local charge neutrality, stoichometry of the compound is assured.

1st Rule

A coordination polyhedron of anions is formed around each cation. The cation-anion distance is the sum of their radii. The coordination number (the number of the anions surrounding the cation) is determined by the ratio of the radii of the two ions. The given coordination number is stable only when the ratio of cation to anion radius is greater than some critical value that provides a bare touching of anions.

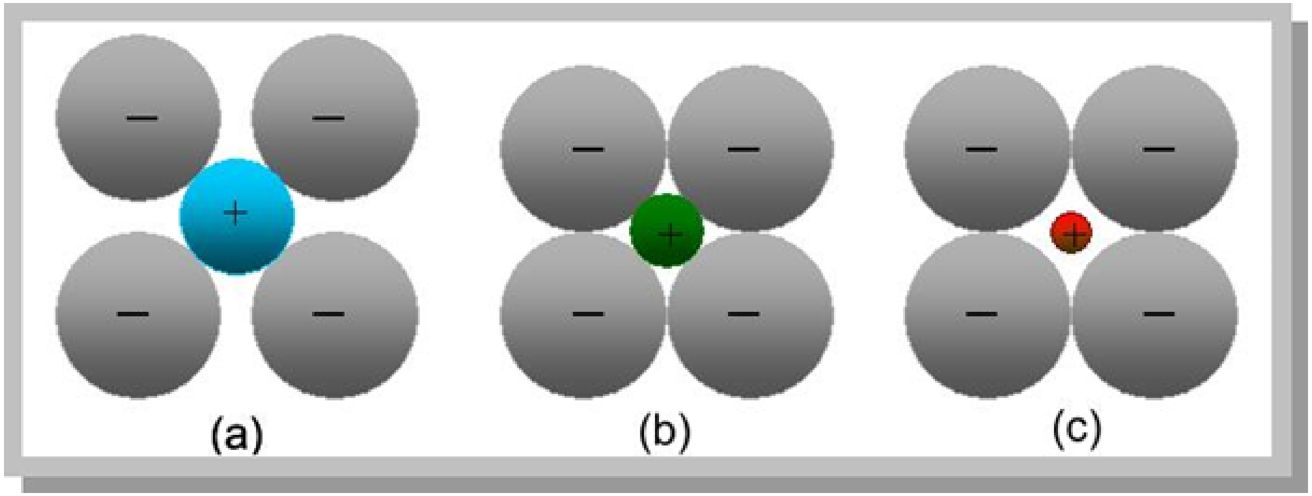
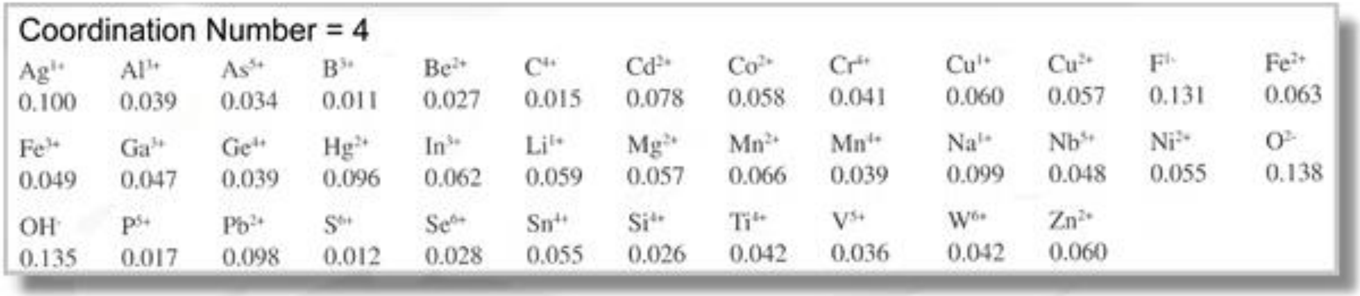


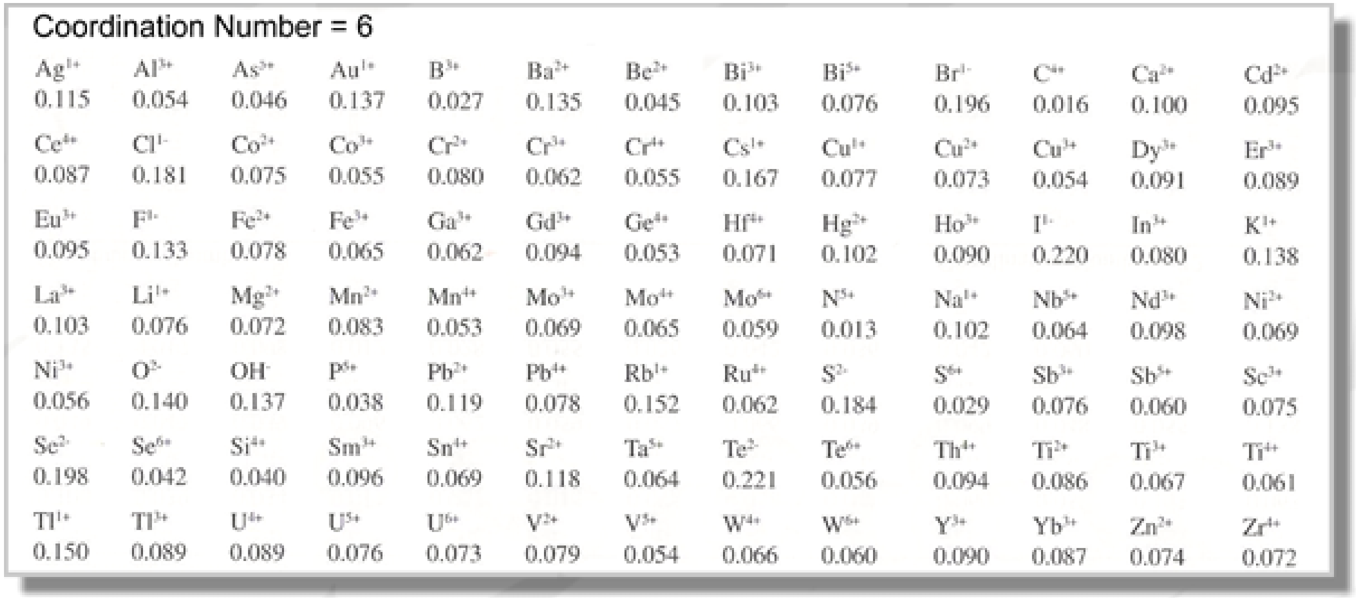
Figure 1.4 stable and unstable coordination configurations. While (a) and (b) are stable, configuration (c) is unstable.

Table 1.2 Ionic Crystal radii (nm)



Coordination Number = 4

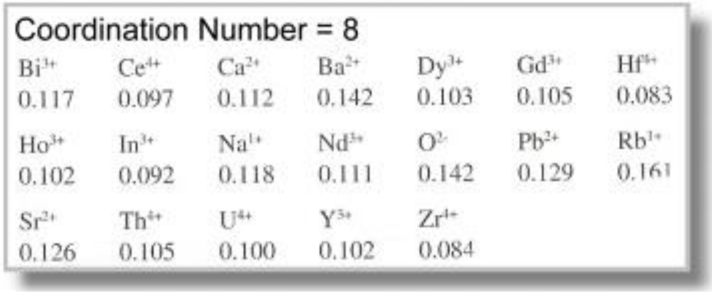
Ag^{1+}	Al^{3+}	As^{5+}	B^{3+}	Be^{2+}	C^{4+}	Cd^{2+}	Co^{2+}	Cr^{4+}	Cu^{1+}	Cu^{2+}	F^{1-}	Fe^{2+}
0.100	0.039	0.034	0.011	0.027	0.015	0.078	0.058	0.041	0.060	0.057	0.131	0.063
Fe^{3+}	Ga^{3+}	Ge^{4+}	Hg^{2+}	In^{3+}	Li^{1+}	Mg^{2+}	Mn^{2+}	Mn^{4+}	Na^{1+}	Nb^{5+}	Ni^{2+}	O^{2-}
0.049	0.047	0.039	0.096	0.062	0.059	0.057	0.066	0.039	0.099	0.048	0.055	0.138
OH^{-}	P^{5+}	Pb^{2+}	S^{6+}	Se^{6+}	Sn^{4+}	Si^{4+}	Ti^{4+}	V^{5+}	W^{6+}	Zn^{2+}		
0.135	0.017	0.098	0.012	0.028	0.055	0.026	0.042	0.036	0.042	0.060		



Coordination Number = 6

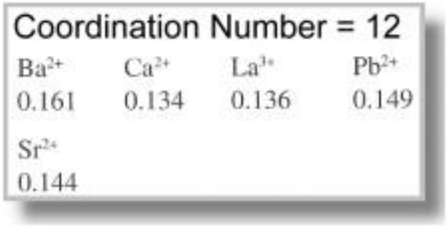
Ag^{1+}	Al^{3+}	As^{5+}	Au^{1+}	B^{3+}	Ba^{2+}	Be^{2+}	Bi^{3+}	Bi^{5+}	Br^{1-}	C^{4+}	Ca^{2+}	Cd^{2+}
0.115	0.054	0.046	0.137	0.027	0.135	0.045	0.103	0.076	0.196	0.016	0.100	0.095
Ce^{4+}	Cl^{1-}	Co^{2+}	Co^{3+}	Cr^{2+}	Cr^{3+}	Cr^{4+}	Cs^{1+}	Cu^{1+}	Cu^{2+}	Cu^{3+}	Dy^{3+}	Er^{3+}
0.087	0.181	0.075	0.055	0.080	0.062	0.055	0.167	0.077	0.073	0.054	0.091	0.089
Eu^{3+}	F^{1-}	Fe^{2+}	Fe^{3+}	Ga^{3+}	Gd^{3+}	Ge^{4+}	Hf^{4+}	Hg^{2+}	Ho^{3+}	I^{1-}	In^{3+}	K^{1+}
0.095	0.133	0.078	0.065	0.062	0.094	0.053	0.071	0.102	0.090	0.220	0.080	0.138
La^{3+}	Li^{1+}	Mg^{2+}	Mn^{2+}	Mn^{4+}	Mo^{3+}	Mo^{4+}	Mo^{6+}	N^{5+}	Na^{1+}	Nb^{5+}	Nd^{3+}	Ni^{2+}
0.103	0.076	0.072	0.083	0.053	0.069	0.065	0.059	0.013	0.102	0.064	0.098	0.069
Ni^{3+}	O^{2-}	OH^{-}	P^{5+}	Pb^{2+}	Pb^{4+}	Rb^{1+}	Ru^{4+}	S^{2-}	S^{6+}	Sb^{3+}	Sb^{5+}	Sc^{3+}
0.056	0.140	0.137	0.038	0.119	0.078	0.152	0.062	0.184	0.029	0.076	0.060	0.075
Se^{2-}	Se^{6+}	Si^{4+}	Sm^{3+}	Sn^{4+}	Sr^{2+}	Ta^{5+}	Te^{2-}	Te^{6+}	Th^{4+}	Ti^{2+}	Ti^{3+}	Ti^{4+}
0.198	0.042	0.040	0.096	0.069	0.118	0.064	0.221	0.056	0.094	0.086	0.067	0.061
Tl^{1+}	Tl^{3+}	U^{4+}	U^{5+}	U^{6+}	V^{2+}	V^{5+}	W^{4+}	W^{6+}	Y^{3+}	Yb^{3+}	Zn^{2+}	Zr^{4+}
0.150	0.089	0.089	0.076	0.073	0.079	0.054	0.066	0.060	0.090	0.087	0.074	0.072

Table 1.2 Ionic Crystal radii (continued)



Coordination Number = 8

Bi^{3+}	Ce^{4+}	Ca^{2+}	Ba^{2+}	Dy^{3+}	Gd^{3+}	Hf^{4+}
0.117	0.097	0.112	0.142	0.103	0.105	0.083
Ho^{3+}	In^{3+}	Na^{1+}	Nd^{3+}	O^{2-}	Pb^{2+}	Rb^{1+}
0.102	0.092	0.118	0.111	0.142	0.129	0.161
Sr^{2+}	Th^{4+}	U^{4+}	Y^{3+}	Zr^{4+}		
0.126	0.105	0.100	0.102	0.084		



Coordination Number = 12

Ba^{2+}	Ca^{2+}	La^{3+}	Pb^{2+}
0.161	0.134	0.136	0.149
Sr^{2+}			
0.144			

2nd Rule:

States that in a stable structure, the total “strength” of the bonds reaching an anion from all surrounding cations should be equal to the charge of the anion. Cation-anion “bond strength” is defined as the valence of the ion divided by the coordination number. That is called: *Rule of the local charge neutrality*.

This rule follows from a consideration of the Coulombic interactions in a crystal. To maximize such interactions we want to maximize the cation-anion interactions, which are attractive, and minimize the anion-anion and cation-cation interactions, which are repulsive. The cation-anion interactions are maximized by increasing the coordination number and decreasing the cation-anion distance. However, we know that if we bring ions too close together electron-electron repulsions become increasingly unfavorable. Thus, optimal cation-anion distances are dictated either by ionic radii or quantitative use of the bond strength rule, which are explained earlier in Pauling's first two rules.

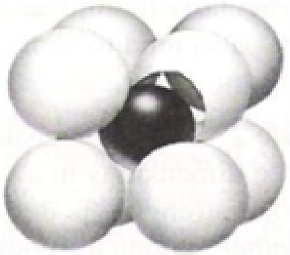
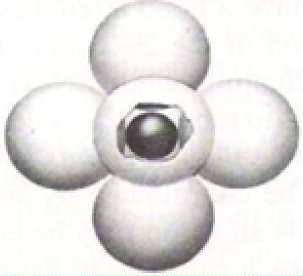
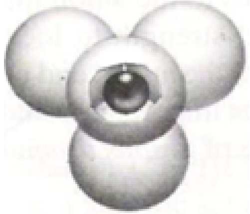
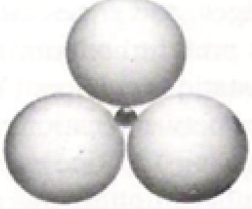
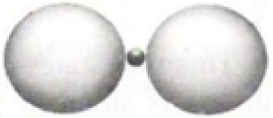
Coordination Number	Disposition of ions about central ion	Cation Radius/Anion Radius	Shapes
8	Corners of Cube	≥0,732	
6	Corners of Octahedron	≥0,414	
4	Corners of Tetrahedron	≥0,225	
3	Corners of Triangle	≥0,155	
2	Linear	≥0	

Figure 1.5Critical radius ratios for various coordination numbers. The most stable structure is the one with maximum coordination number allowed by the radius ratio.

3rd Rule:

In a stable structure the corners, rather than the edges and especially the faces, of the coordination polyhedra tend to be shared. Also, if an edge has to be shared, it tends to be shortened.

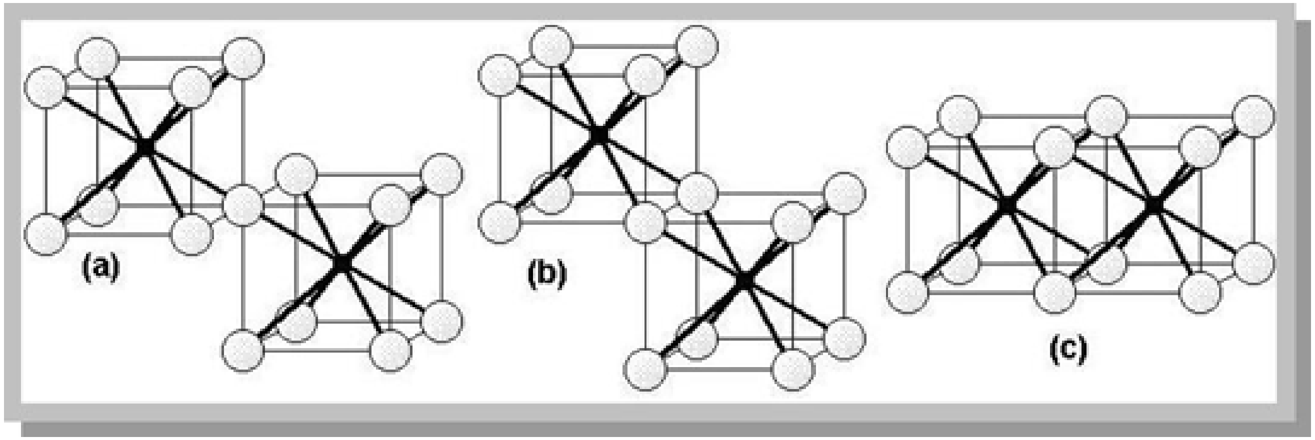


Figure 1.6 a) the most favorable linking of polyhedra; b) edge-sharing; c) face-sharing (the least favorable linking of polyhedra). If an edge has to be shared, it tends to be shortened.

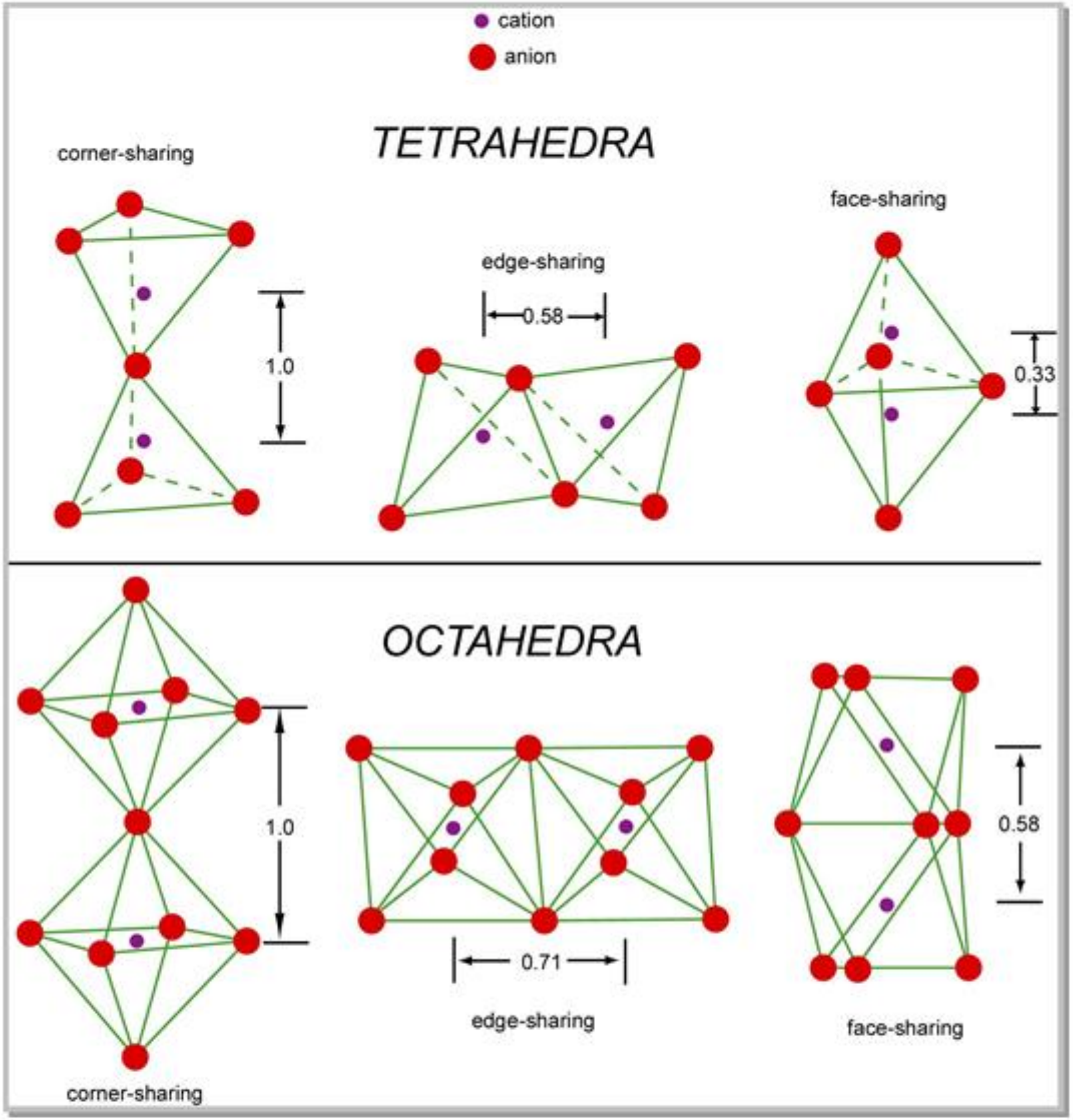


Figure 1.7 Tetrahedra and octahedra linked by sharing (a) corner, (b) edge, (c) face

4th Rule:

Rule 3 becomes more important when the coordination number (CN) is small and the valence of ions is high.
Poly-hedra formed around cations of low coordination number and high charge tend especially to be linked by corner sharing

5th rule:

states that the number of different ions in a structure tends to be small; due to the difficulty to efficiently pack ions and coordination polyhedra in a single structure.
In other words, high number of constituents causes phase seperation. So, simple structures are preferred over more complicated arrangements.

Bringing an ion and a cation together, ends with ionic bonding. The molecules formed by ionic bonding tend to get together with other ionic molecules. This gathering is a tendency to form crytals. In the formation of stable crystals, the measure of stability is important. Madelung constant, α comes on the scene at that point.

α: a constant for a certain structure which is determined by coordinating anions around o certain cation or vice versa (Pauling Rule). How can we bring together these coordinations of cations and anions over large distance and create crystals with periodic arrays of atoms or molecules?
For ionic crystals or metals, visualization may be simpler. Both with spherical symetry in their building blocks (ions or metal ions) can be imagined as "hard balls". If stacking of balls (either of equal size or different sizes) can end up with high packing density, high packing density usually means a stable crystal structure.

2. Structures of Ceramics

Packing in Ionic Crystals

Simple cubic packing

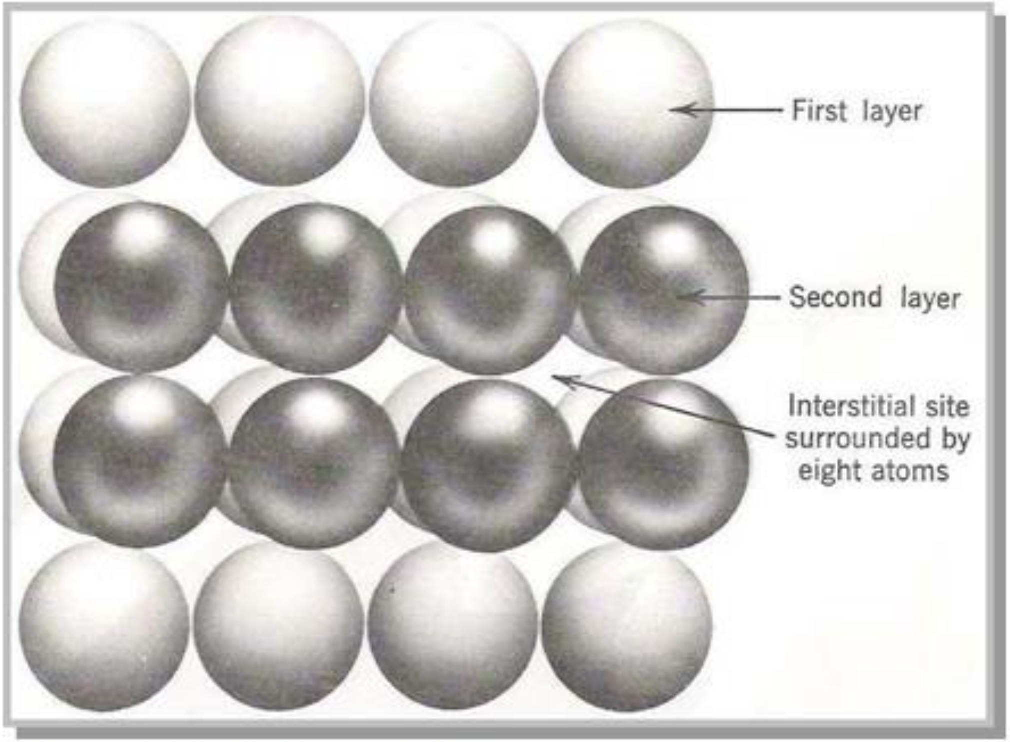


Figure 2.1 Simple cubic packing of spheres

Closed Packed Structures:

Closed Packed Cubic

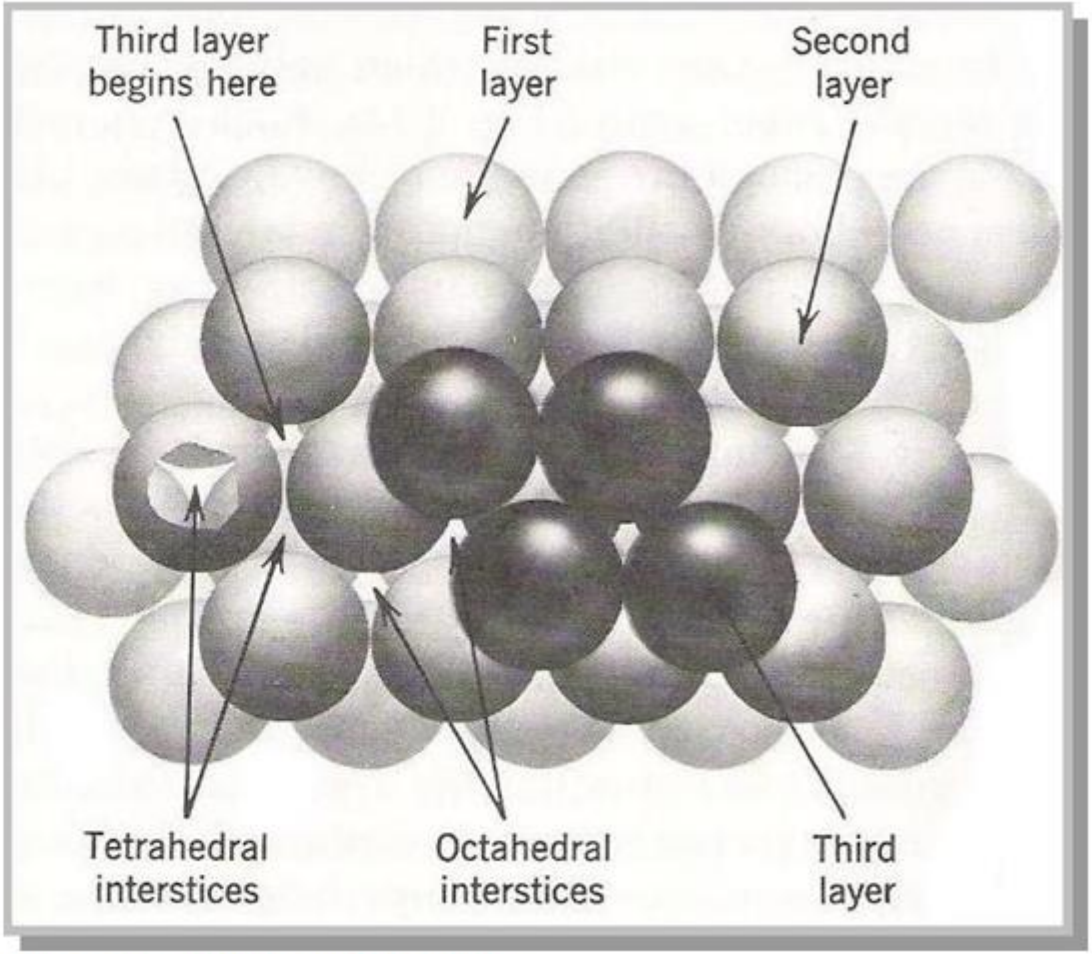


Figure 2.2 Face Centered Cubic packing of spheres

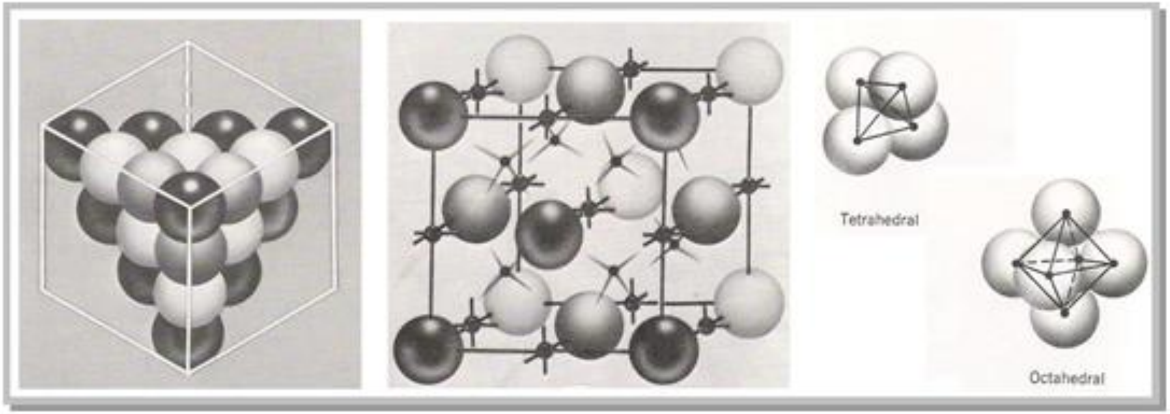


Figure 2.3 Various aspects of FCC

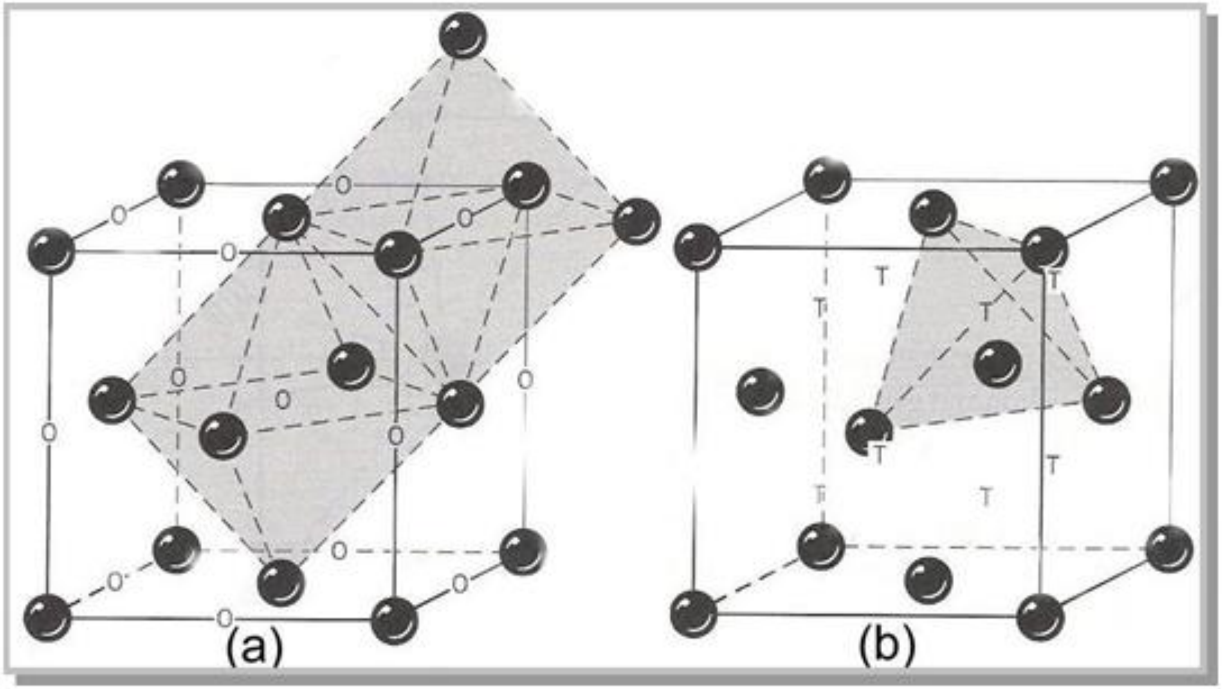


Figure2.5 (a)Octahedral Sites (O) in FCC. The body-centered site and edge site are outlined. (b) tetrahedral sites (T) in FCC. There is one within each corner, and together they form a simple cubic array.

Hexagonal Closed Packed Structure

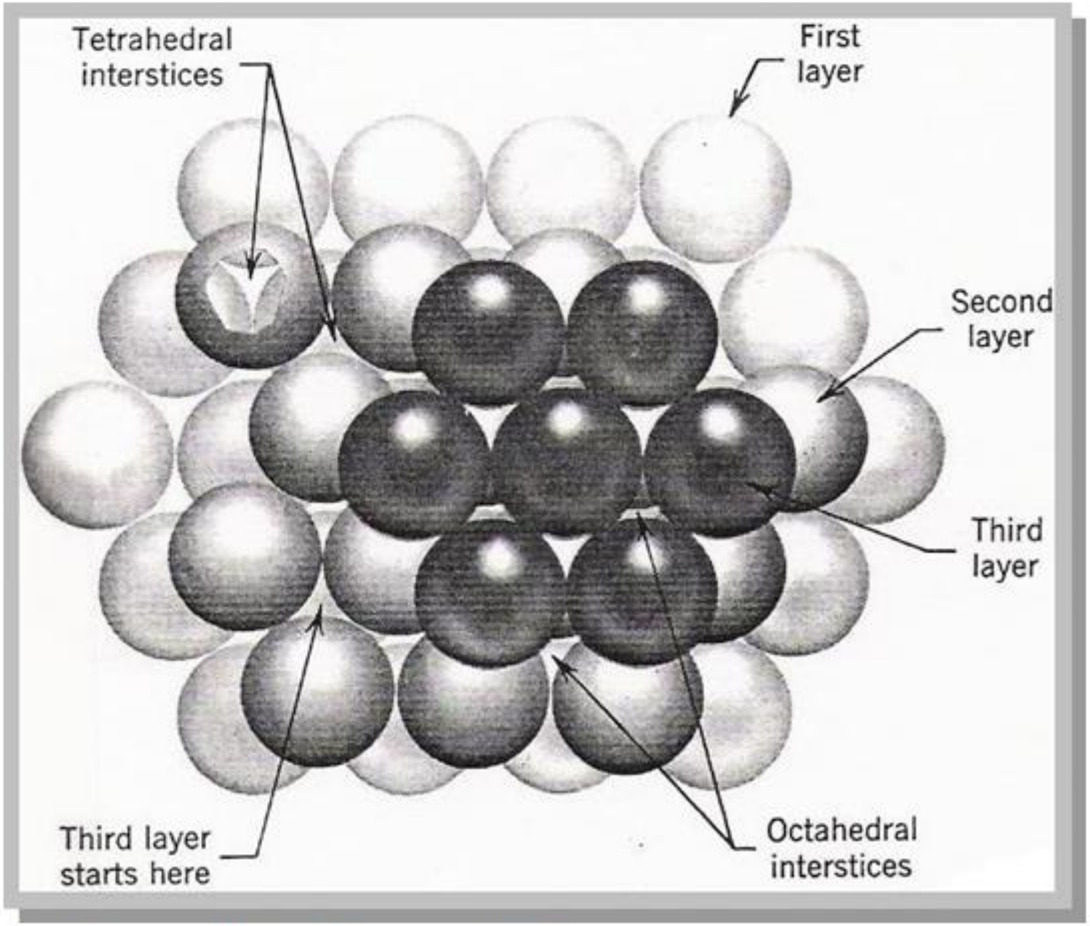


Figure 2.6 Hexagonal Closed Packed Structure (HCP)

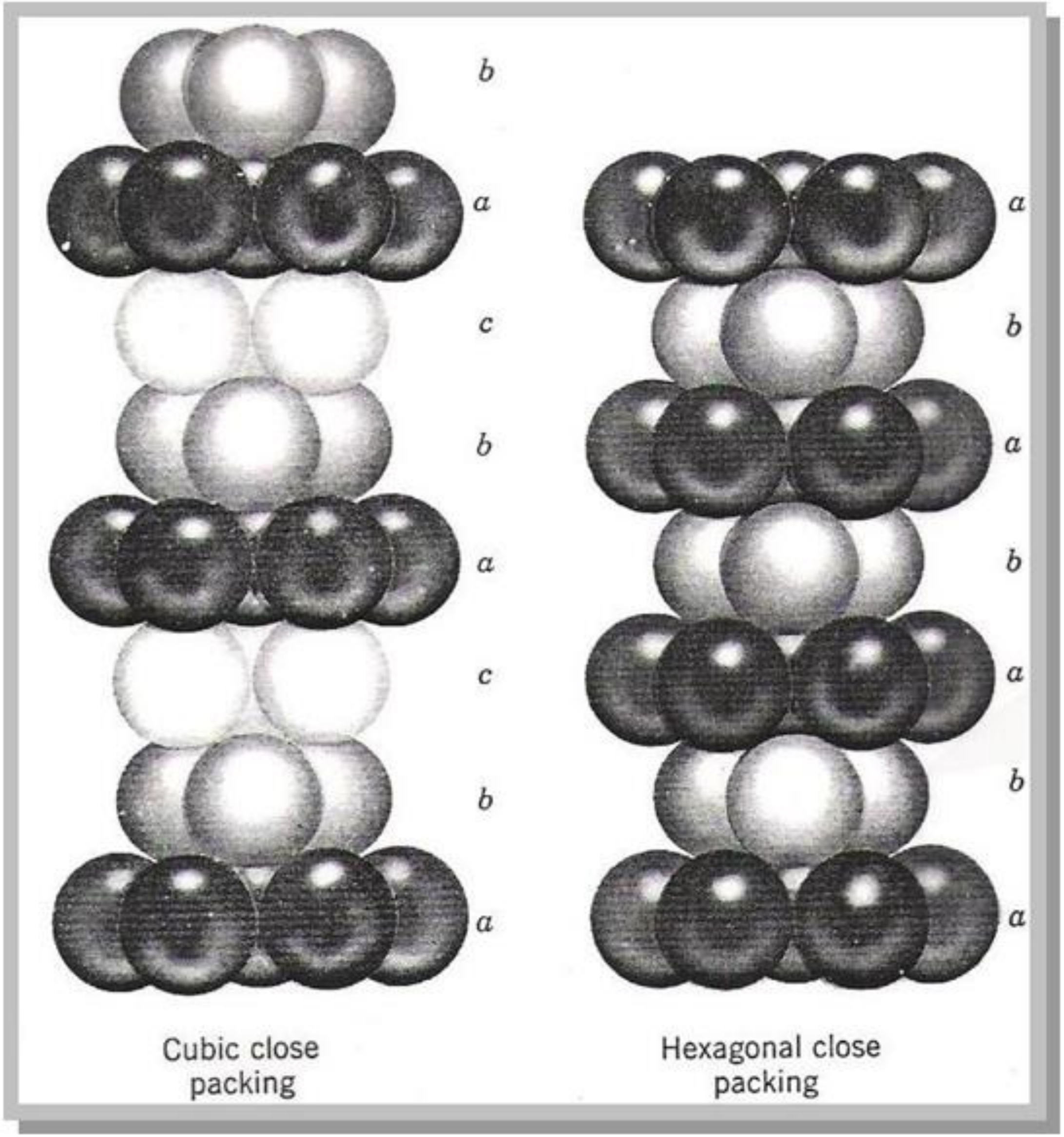


Figure 2.7 Development of hexagonal close packing

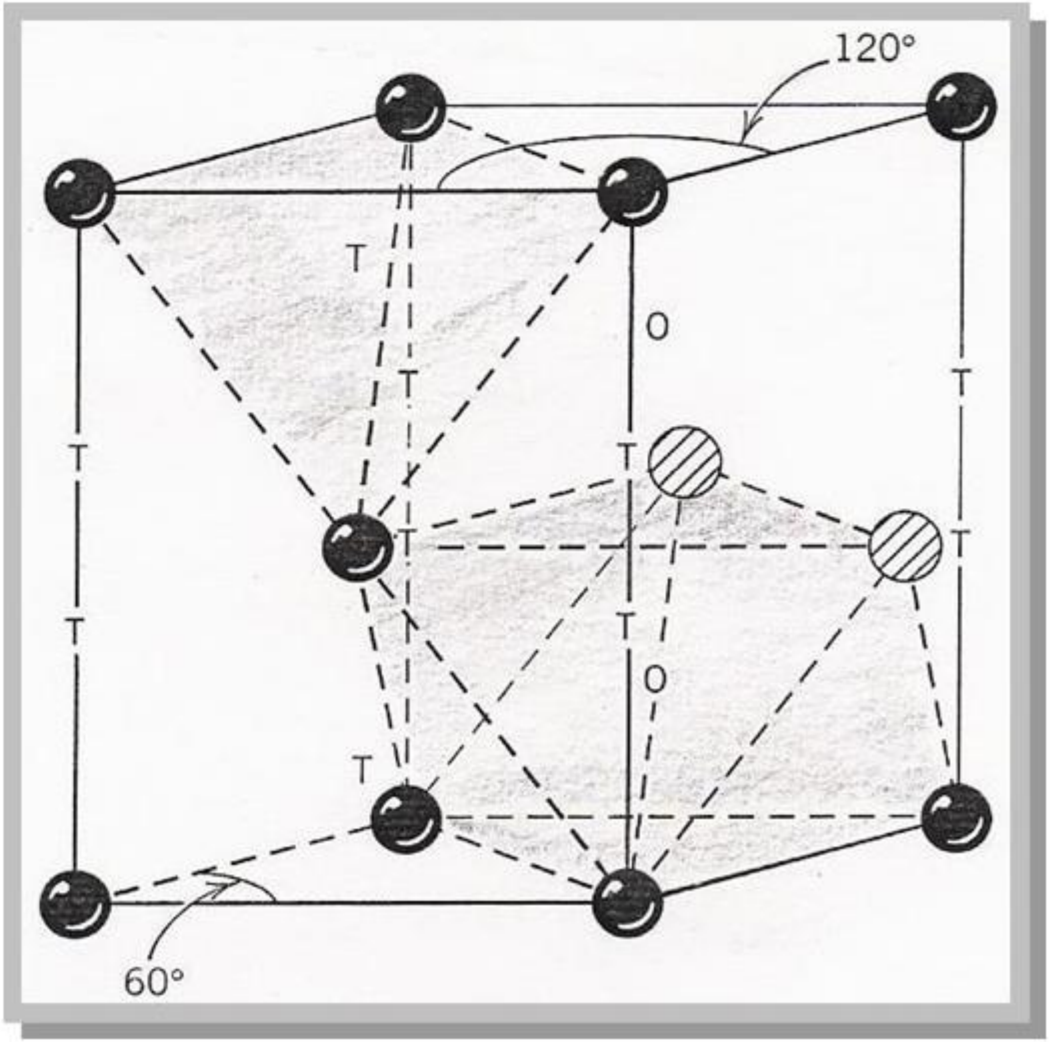


Figure 2.8 Location of tetrahedral sites (T) and Octahedral sites (O) in HCP. Dotted lines show one of each type.

Ceramic Structures for ionic crystals

Crystal Structures of Oxides (Structures based on oxide close packing)

CsCl-type structures

CsCl with its huge cation trying to fit between equally large anions crystallize in simple cubic (SC) structure.
The ionic radii ratio is

$r_{Cs^+}/r_{Cl^-} = 170/181 = 0.94 \geq 0.732$ therefore an 8-fold coordination of Cs ions with chlorine ions is preferred; vs verce for the chlorine ions. Each arm is 1/8 strong from both sides.

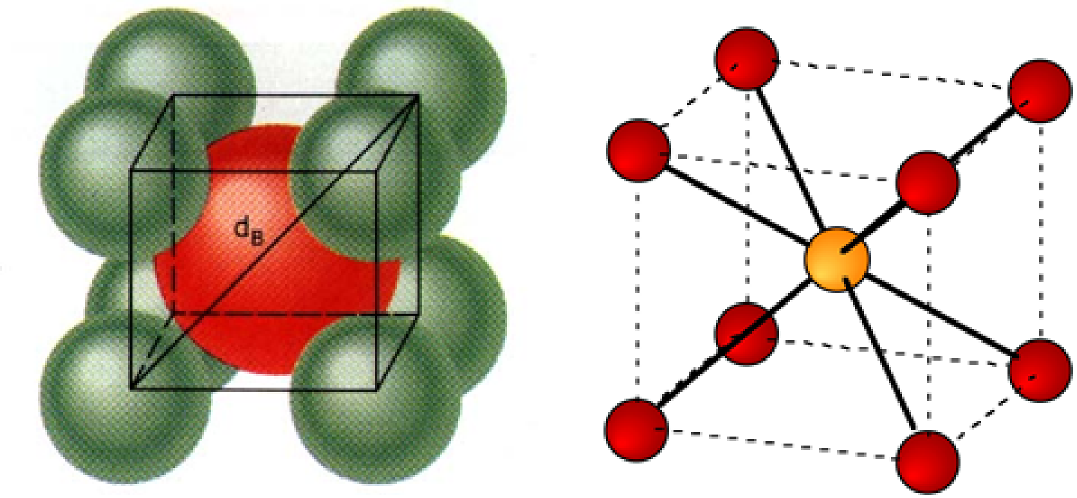


Figure 2.11a CSCl unit cell with eigh-fold coordination of both ions.

There are several in this non-directional bonding arrangement some intermatellic like NiAl and some halides like CsBr, CsI, TlCl, and TlBr are found.
Their infrared, visible and UV transmittance is remarkable.
Halides are particularly important for their IR transmittance.

FCC- based ceramic structures

Rocksalt structure: MX

A typical example: NaCl

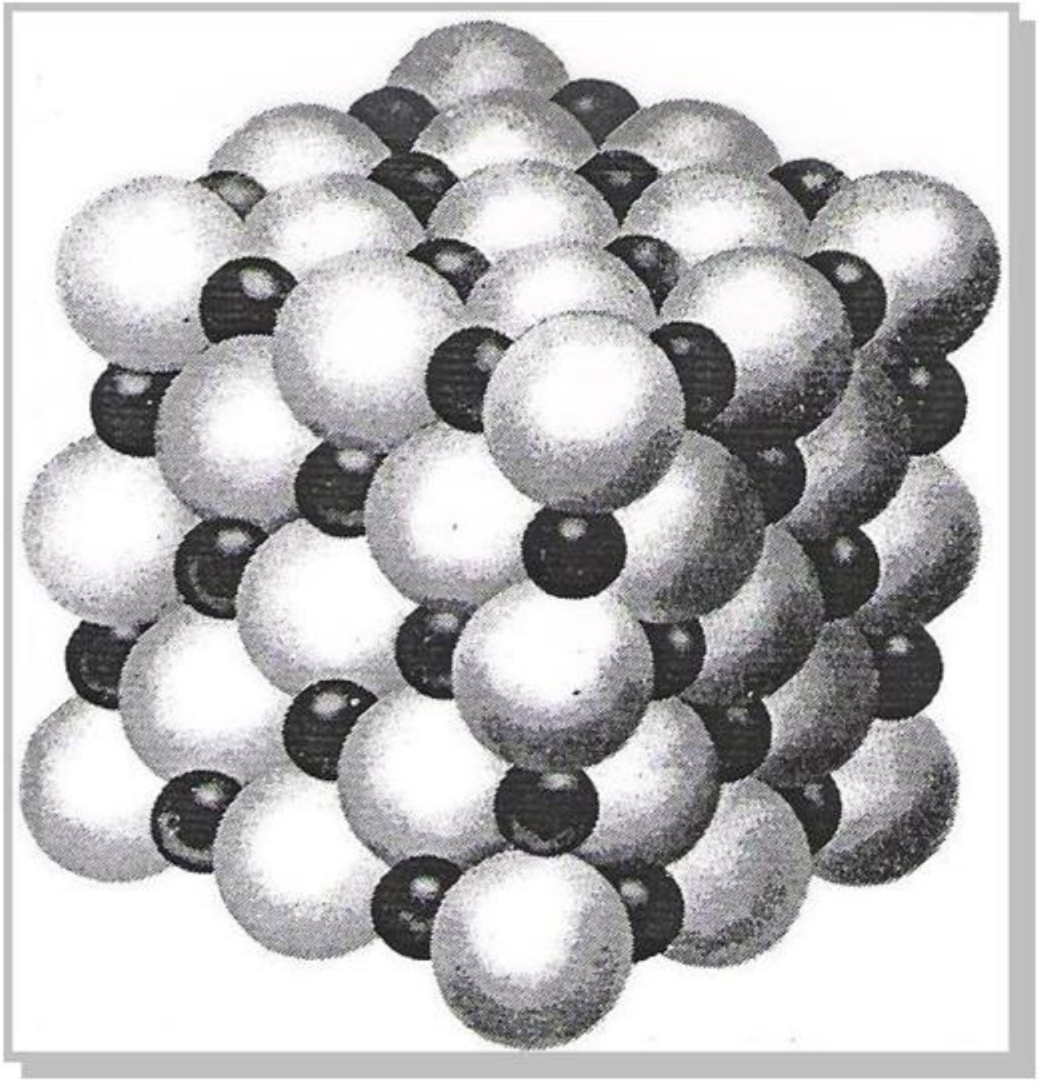


Figure 2.12 Crystal structure of sodium chloride.

Table 2.2 Some ceramic crystal structures

Structure	Stoichiometry	Anion Packing	Coordination Number around M and X	Examples	Derivative Structures
Rocksalt	MX	FCC	6, 6	NaCl, KCl, LiF, KBr, MgO, CaO, SrO, BaO, NiO, CoO, MnO, FeO, TiN, ZrN	
Zincblende	MX	FCC	4, 4	ZnS, SiC (3C), BN, GaAs, CdS, InSb	Diamond cubic (Si, Ge, C)
Wurtzite	MX	HCP	4, 4	ZnO, ZnS, AlN, SiC (2H), BeO	
Nickel arsenide	MX	HCP	6, 6	NiAs, FeS, FeSe, CoSe	
Anti-fluorite	M_2X	FCC	4, 8	Li_2O, Na_2O, K_2O, Rb_2O	
Fluorite	MX_2	Primitive Cubic	8, 4	CaF_2, ZrO_2, UO_2, ThO_2, CeO_2	Pyrochlore ($A_2B_2O_7$), e.g., $Pb_2Ru_2O_7$, $Gd_2Ti_2O_7$, $Gd_2Zr_2O_7$ Bixbyite (e.g. Y_2O_3)
Cesium Chloride	MX	Primitive Cubic	8, 8	CsCl, CsBr, CsI	
Rutile	MX_2	Distorted HCP	6, 3	TiO_2, SnO_2, GeO_2 MnO_2, VO_2, NbO_2 RuO_2, PbO_2, PbO_2	Defective ''Magneli phases'' of formula Ti_nO_{2n-1}
Corundum	M_2X_3	HCP	6, 4	Al_2O_3, Cr_2O_3	Ilmenite ($FeTiO_3$) Lithium Niobate ($LiNbO_3$, $LiTaO_3$)
Perovskite	ABX_3	AO sublattice forms FCC	12, 6, 6	$CaTiO_3$, $SrTiO_3$ $BaTiO_3$, $PbTiO_3$ $LaGaO_3$, $LaAlO_3$ $BaZrO_3$, $PbZrO_3$ $Ba(Pb_{1-x}Bi_x)O_3$, $Ba_{1-x}K_xO_3$ $Pb(Zr, Ti)O_3$ $(Pb, La)(Zr, Ti)O_3$	Ordered solid solutions, e.g., $Pb(Mg_{1/3}Nb_{2/3})O_3$, $Pb(Sc_{1/2}Ta_{1/2})O_3$
Spinel	AB_2X_4	FCC	4, 6, 4	$MgAl_2O_4$, $FeAl_2O_4$ $ZnAl_2O_4$, $ZnFe_2O_4$ $MnFe_2O_4$, $LiTi_2O_4$	Many solid solutions are possible.
Inverse spinel	$B(AB)X_4$	FCC	4, 6, 4	Fe_3O_4, $CoFe_2O_4$ $NiFe_2O_4$, $MgFe_2O_4$	Many solid solutions.
"K_2NiF_4"	A_2BX_4	Alternating perovskite and rocksalt type layers	9, 6, 6	K_2NiF_4, La_2CuO_4 $La_{2-x}Sr_xCuO_4$, La_2NiO_4	"Ruddlesden-Popper" phases $AO \cdot nABO_3$, e.g., Sr_2TiO_4, $Sr_3Ti_2O_7$; high temperature oxide superconductors of formula $mAO \cdot nABO_3$ such as $Bi_2Sr_2CaCu_2O_8$, $Tl_2Ba_2Ca_2Cu_3O_{10}$.
"$YBa_2Cu_3O_7$"	$AB_2C_3X_7$	Perovskite-like with missing oxygens	8, 10, 5 or 4, 6	$YBa_2Cu_3O_7$, $MBa_2Cu_3O_7$, where M = Eu, Dy, Ho, Er, Yb	$Y_2Ba_4Cu_7O_x$, $Y_2Ba_4Cu_8O_x$
Silicates (quartz, tridymite crystobalite)	AX_2	Corner-shared SiO_4 tetrahedra	4, 2	SiO_2, GeO_2	β-eucryptite ($LiAlSiO_4$) is a quartz derivative; many other crystalline silicates of similar coordination; network glasses.
Silicon nitride	A_3X_4	Corner shared SiN_4 tetrahedra	4, 3	α- Si_3N_4, β-Si_3N_4	Silicon oxynitrides solid solutions (sialons) with valence-compensating cation and anion substitutions.

Antifluorite and Fluorite structure: M_2X or MX_2

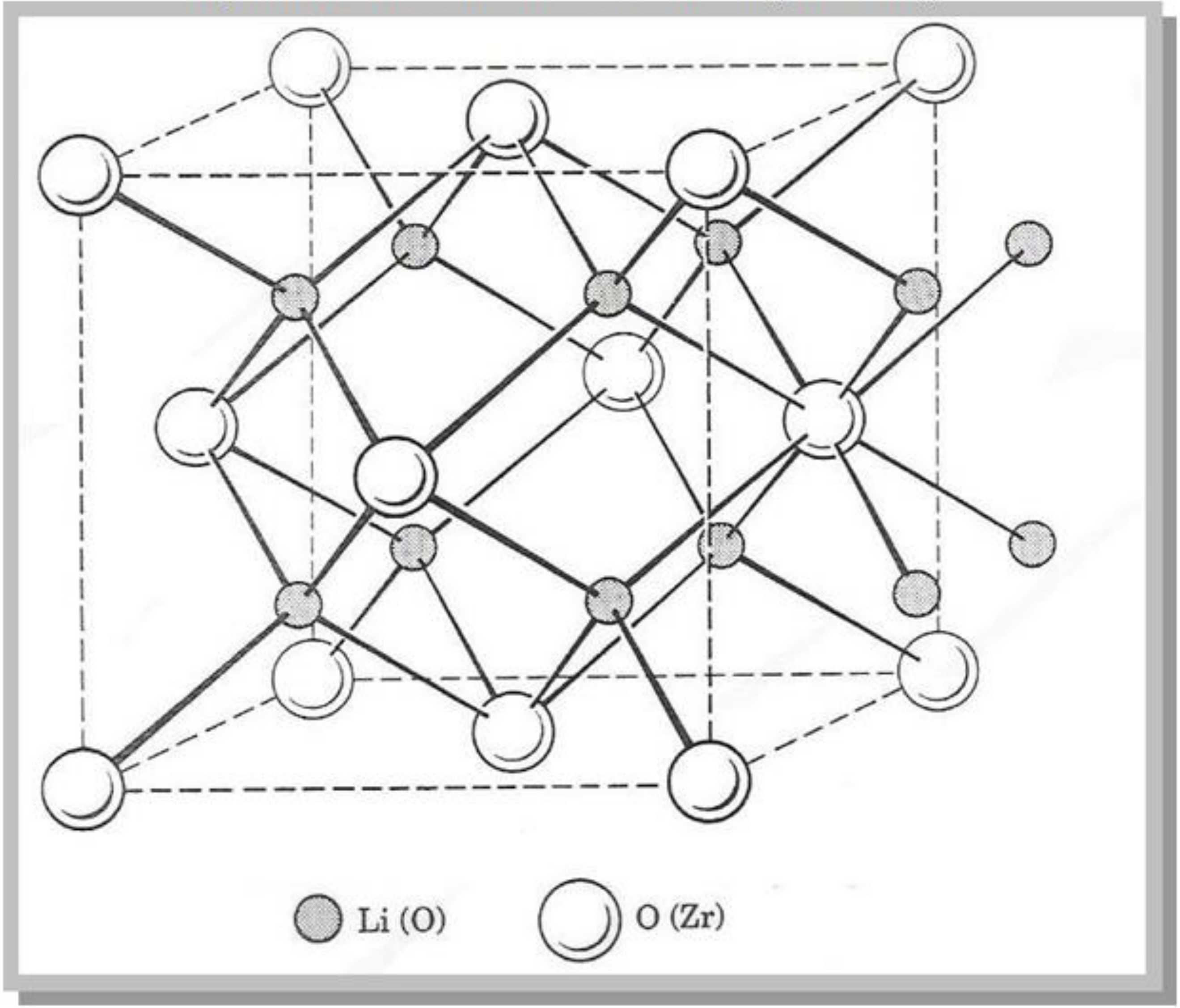


Figure 2.14 Antifluorite or Fluorite structure

Typical examples: CaF_2 (Fluorite)
Na_2O (Anti-Fluorite)

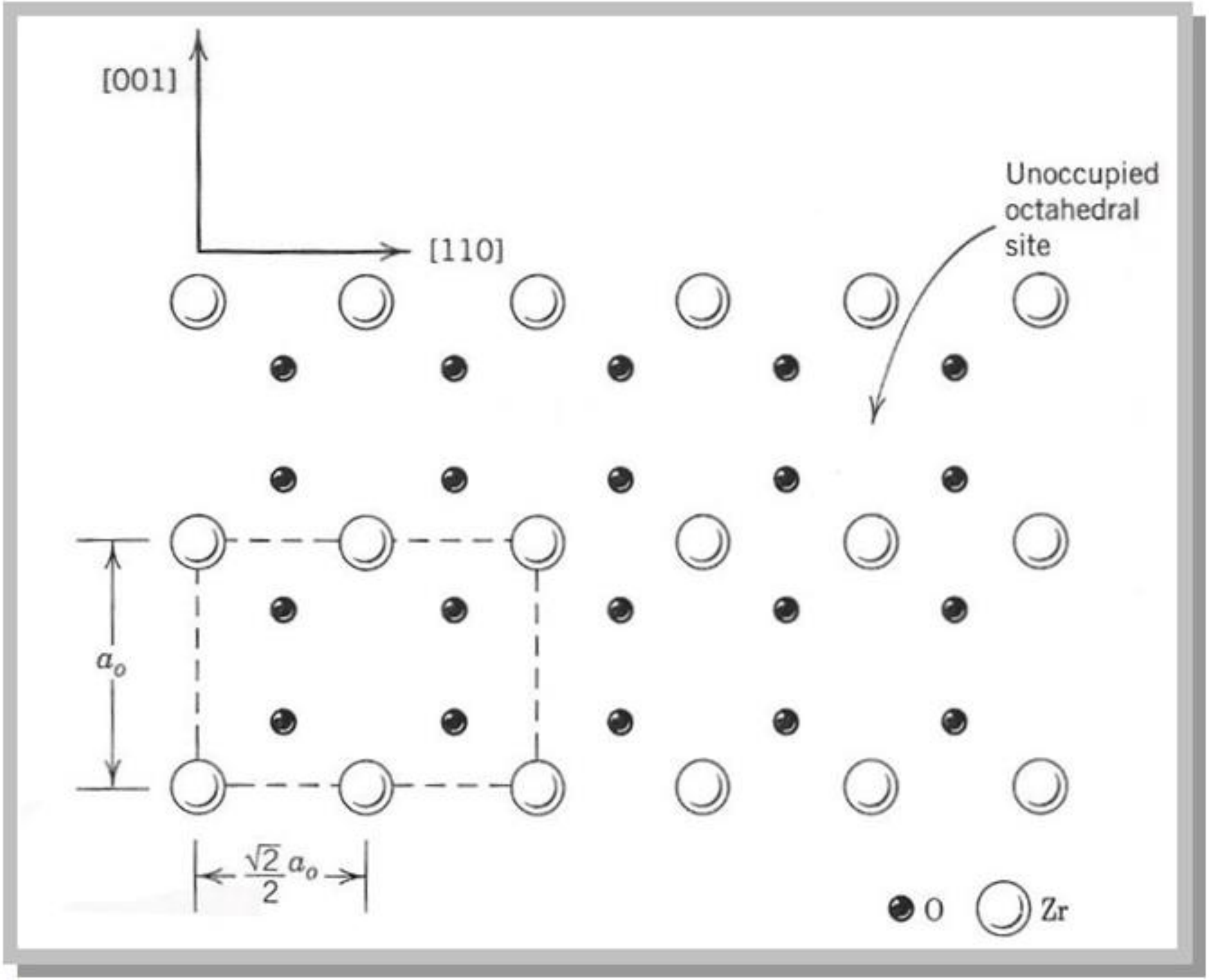


Figure 2.15 (110) plane of the fluorite structure cmpound ZrO_2.

Typical examples: Ni_2O, Na_2O, K_2O (Antifluorite)
ZrO_2, UO_2, ThO_2, CeO_2, TeO_2, CaF_2 (Fluorite)

Zincblende structure: MX (with smaller cations)

r_{Ca}^{+} / R_{an} require a tetrahedral coordination but the stoichiometry is AB → anions got to atom positions; cations go to half of the tetrahedral interstices.

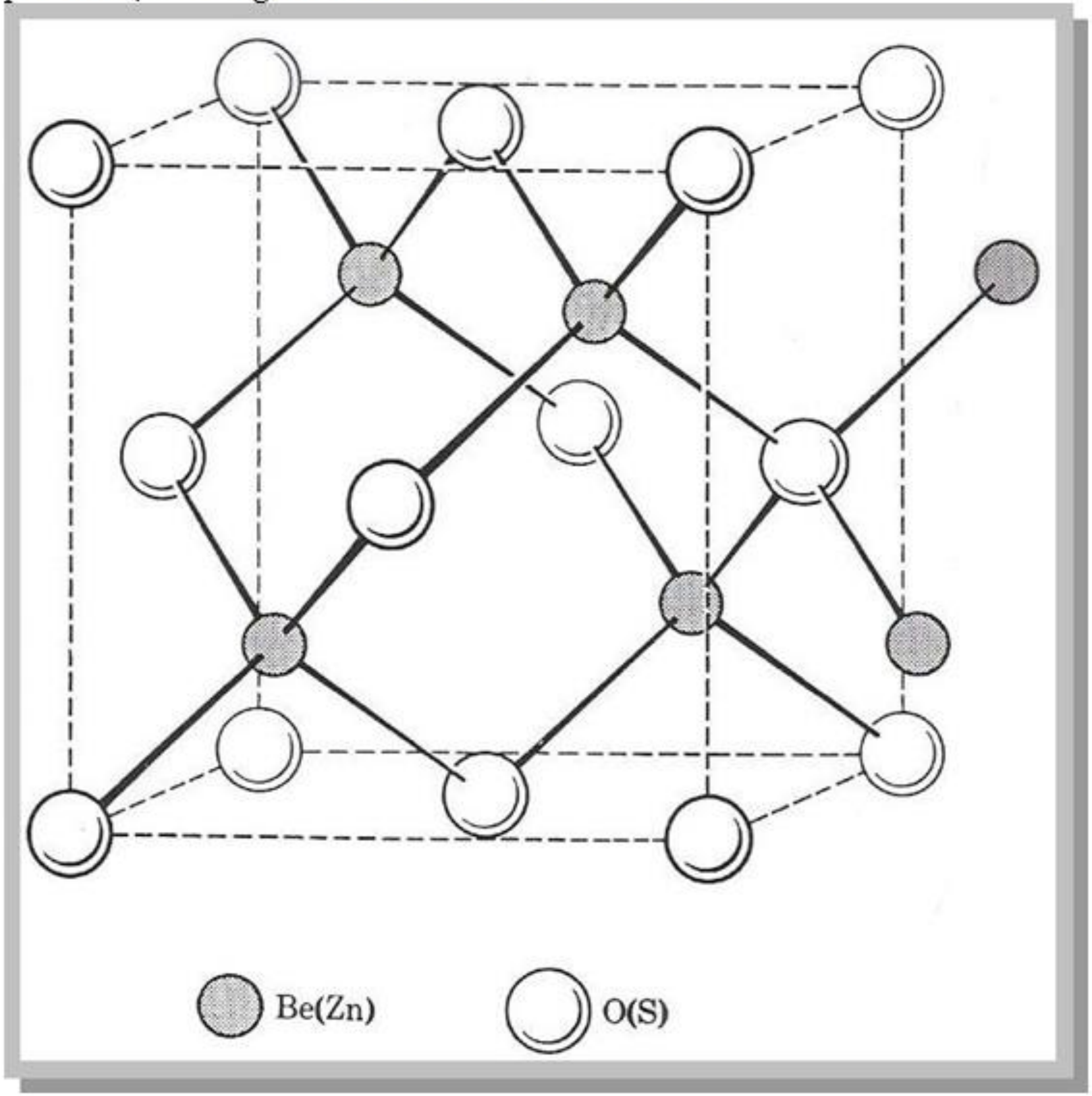


Figure 2.16 Zincblende (ZnS) structure

To maximize cations separation, half of the tetrahedral interstitial sites on opposing corners of the unit cell are filled.

→ the tetrahedral share only corners

Quite some numbers of covalently bonded compounds also choose zincblende structure, like SiC, BN, GaAs with tetragonal directionality. These are the compounds that form through sp^3 hybridized orbitals.

Example Compound: ZnO, ZnS, BeO, CdS, GaP, InSb

Many compounds of zincblende structure may also form wurtzite structure with only stacking being different.

A related structure to zincblende is the diamond structure: (With only one kind of atoms)

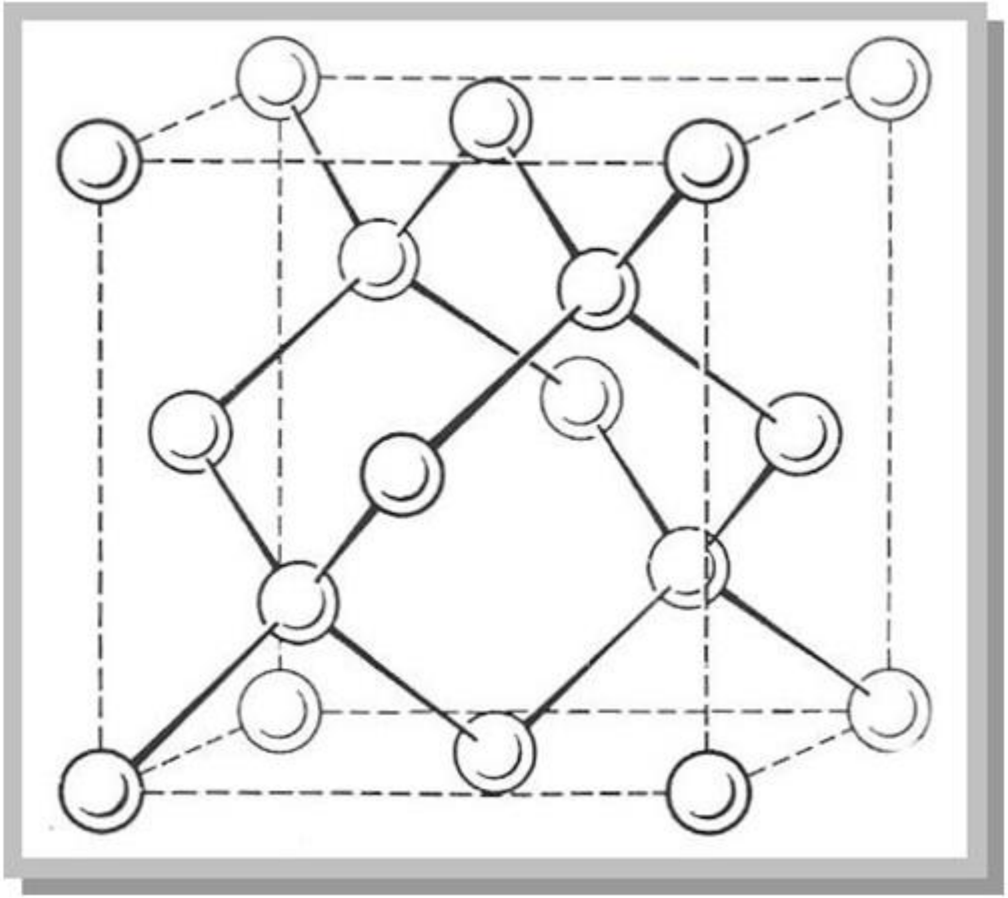


Figure 2.17 Crystal structure of diamond

HCP-based Ceramic Structures

Wurtzite: MX

Very closely related to FCC Zincblende (ZnS) is wurtzite (ZnO) structure with a very close stability to Zincblende's: Madelung constants: $\alpha_{zincblende} = 1.638$

$\alpha_{wurtzite} = 1{,}641$

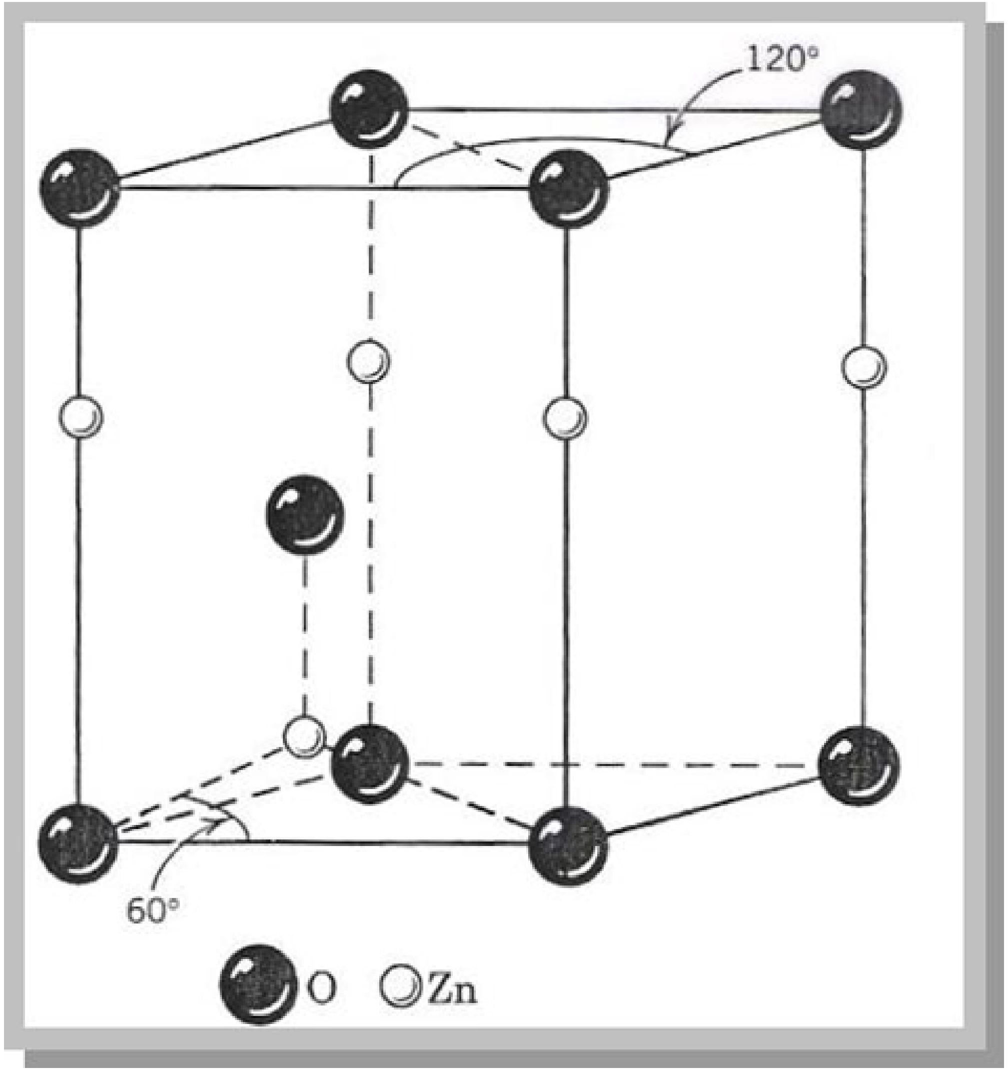


Figure 2.18 Unit cell of the wurtzite structure.

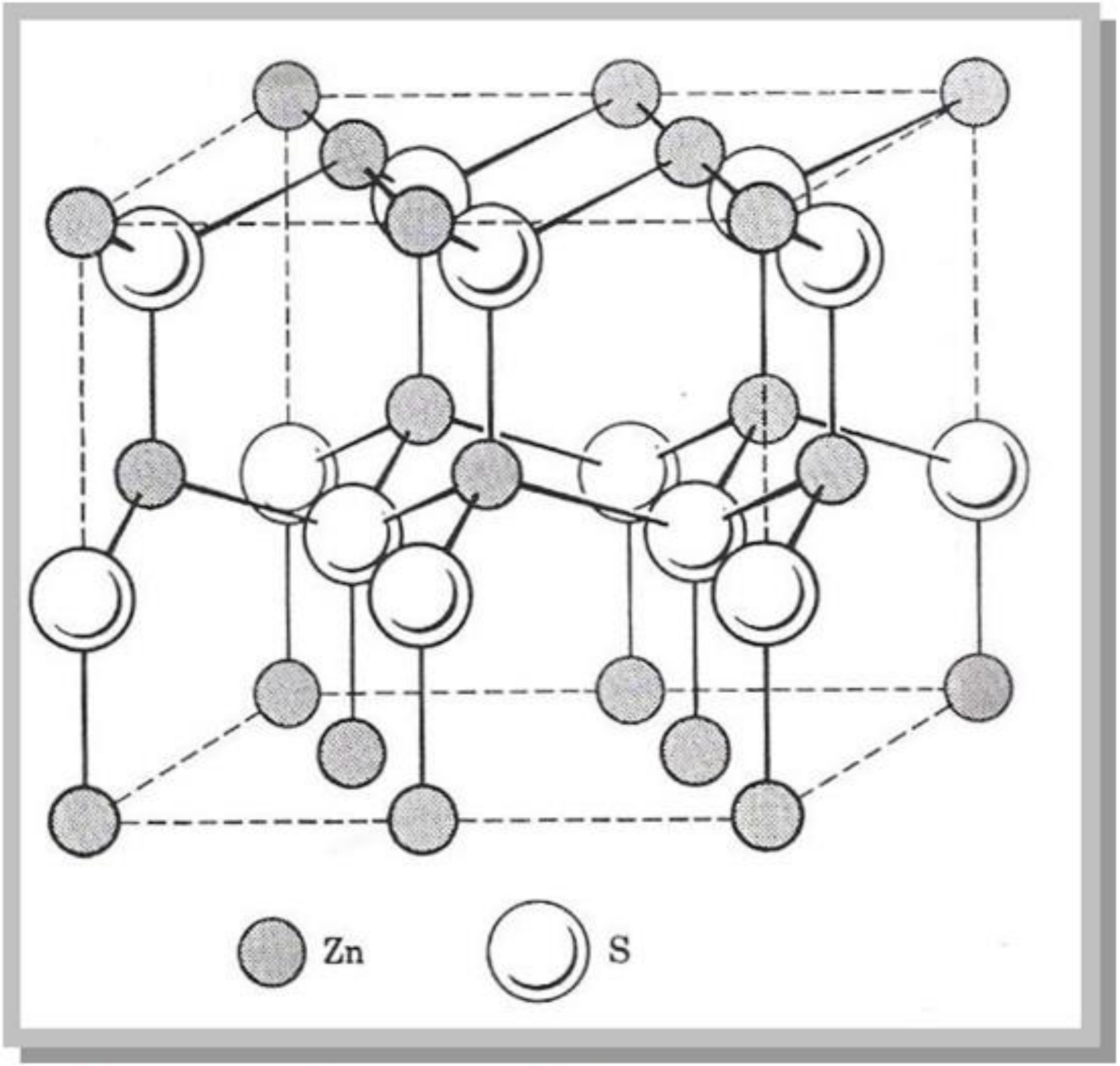


Figure 2.19 Wurtzite (ZnS) structue (also BeO)

In wurtzite too, cations occupy half of the available tetrahedral interstitial sites, of one kind (either all with apex "up" or all with apex "down") to maximize cation cation distance. Again cation and anion coordination is mutually 4-fold tetrahedral share corners only. Zincblende and wurtzite are polymorphs and polytypes.

Corundum Structure: M_2O_3

Another common crystal structure based on HCP packing (anion packing) is corundum structure. (after Al_2O_3, a.k.a. aluminum oxide, α-alumina, sapphire (single crystalline Al_2O_3)) [*Sapphire is basis for Ruby, blue sapphires, star sapphires].

In corundum structure; due to 2:3 cation to anion ratio, and $r_{Al^{+3}} / R_{O^{-2}}$ ratio there is an octahedral coordination of Al^{+3} by O^{-2} ions. So, cations fill 2/3 of all available octahedral interstices in HCP of oxygens.

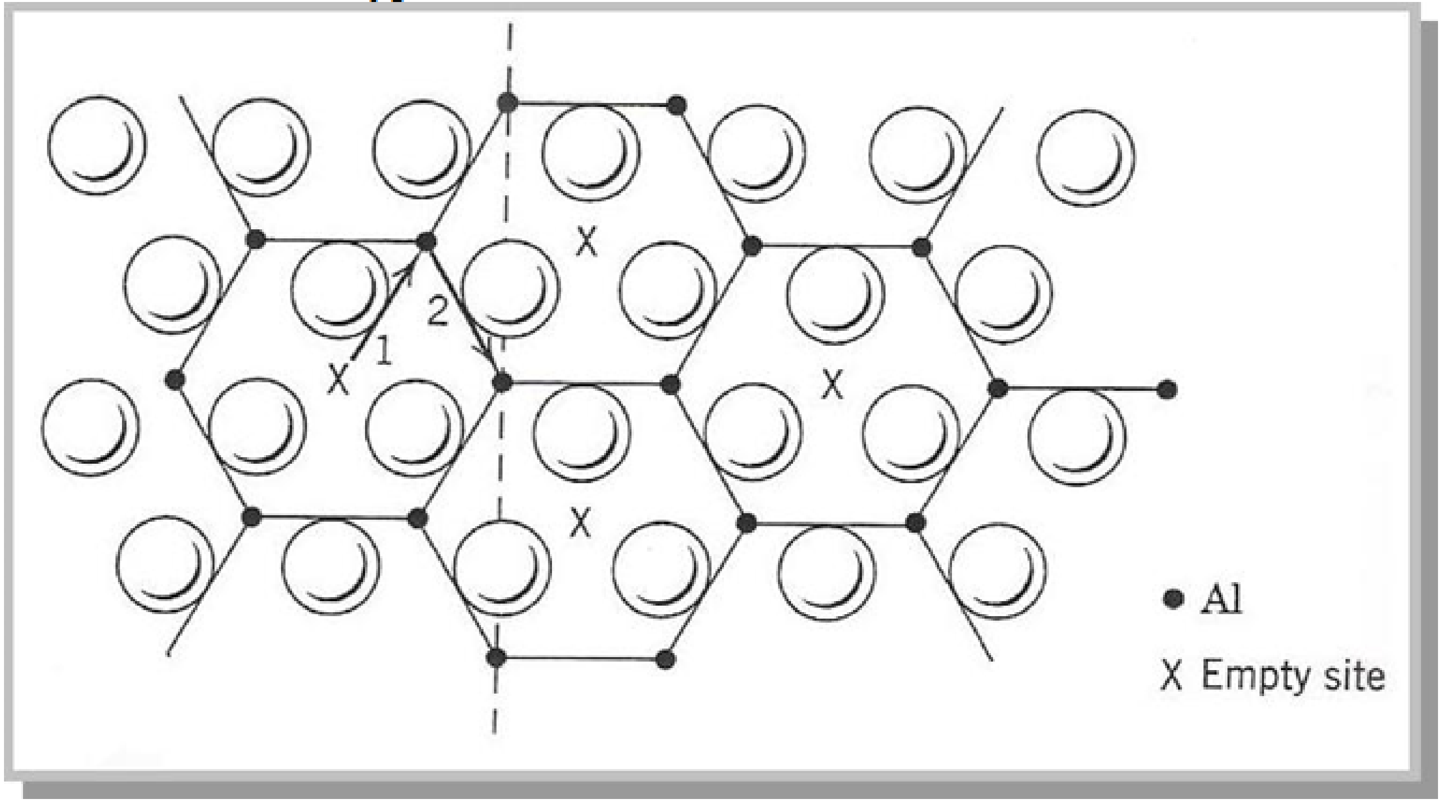


Figure 2.20 Filling of 2/3 of the octahedral sites in the basal plane of corundum. Only one close packed anion plane is shown.

In order to have a maximum cation seperation in a symmetrical order, the empty 1/3 octahedral sites are shifted by one atomic spacing in each neighboring layer in C direction.

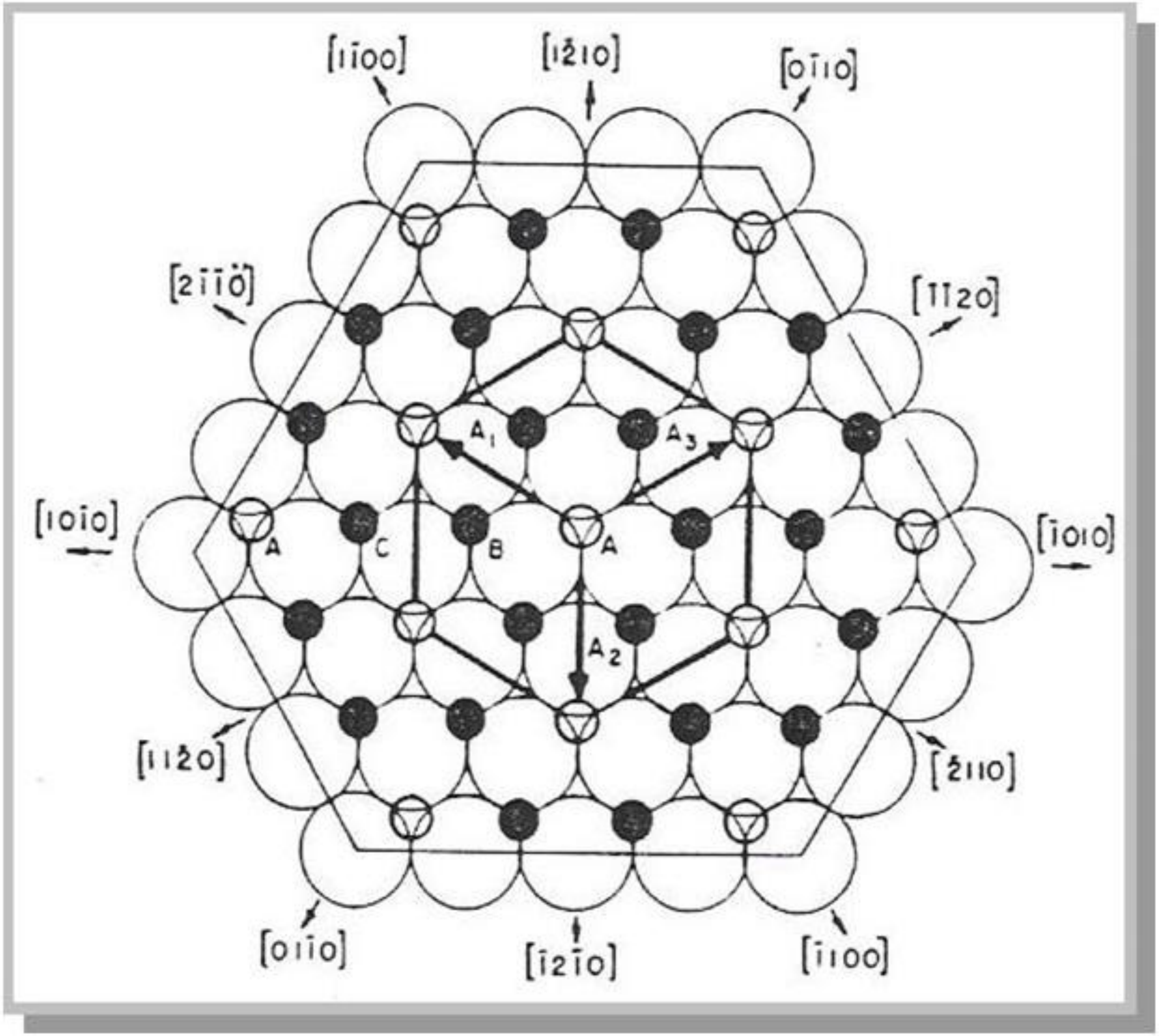


Figure 2.22 The basel plane of Sapphire, showing the hexagonal close-packed anion sublattice and the cations occupying two-thirds of the octahedral interstices.

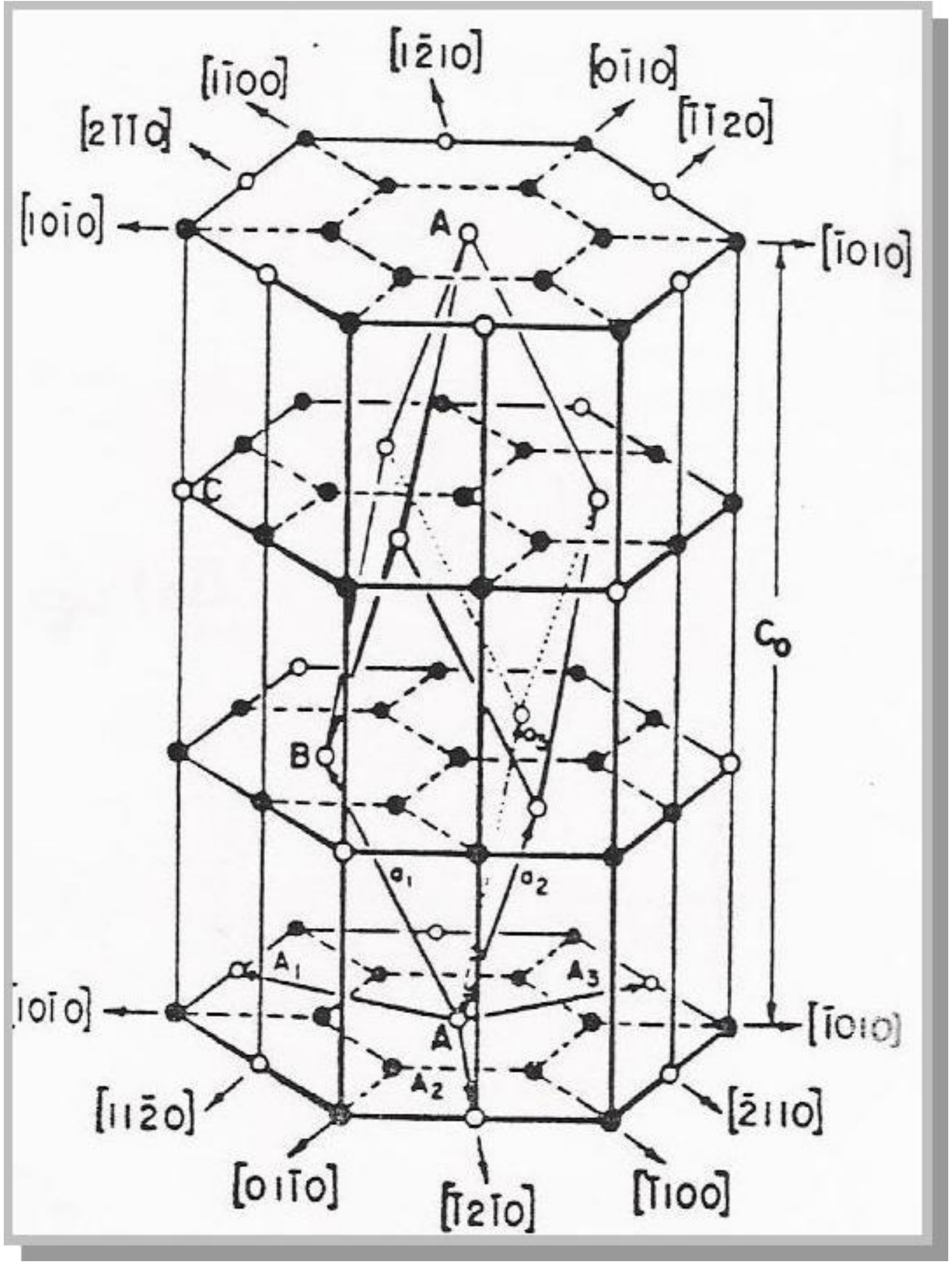


Figure 2.23 The cation sublattice in sapphire. The vacant octahedral sites define the corners of a morphological unit cell.

Al^{+3} in octahedral coordination with oxygens, oxygen has 4 Al^{+3} around it.

Besides Al_2O_3, Cr_2O_3, Fe_2O_3 also crystallize in corundum structure (interestingly Cr^{+3} and Fe^{+3} are the only cations that have a significant solubility in Al_2O_3.)

$FeTiO_3$ (ilmenite) and $LiNbO_3$ are also derived from corundum structure type.

These are structures where both cations prefer octahedral interstices. In ilmenite alternating cation layers are filled by Fe or Ti alone.

In $LiNbO_3$, each basal layer has equal number of Lithium and Niobium cations.

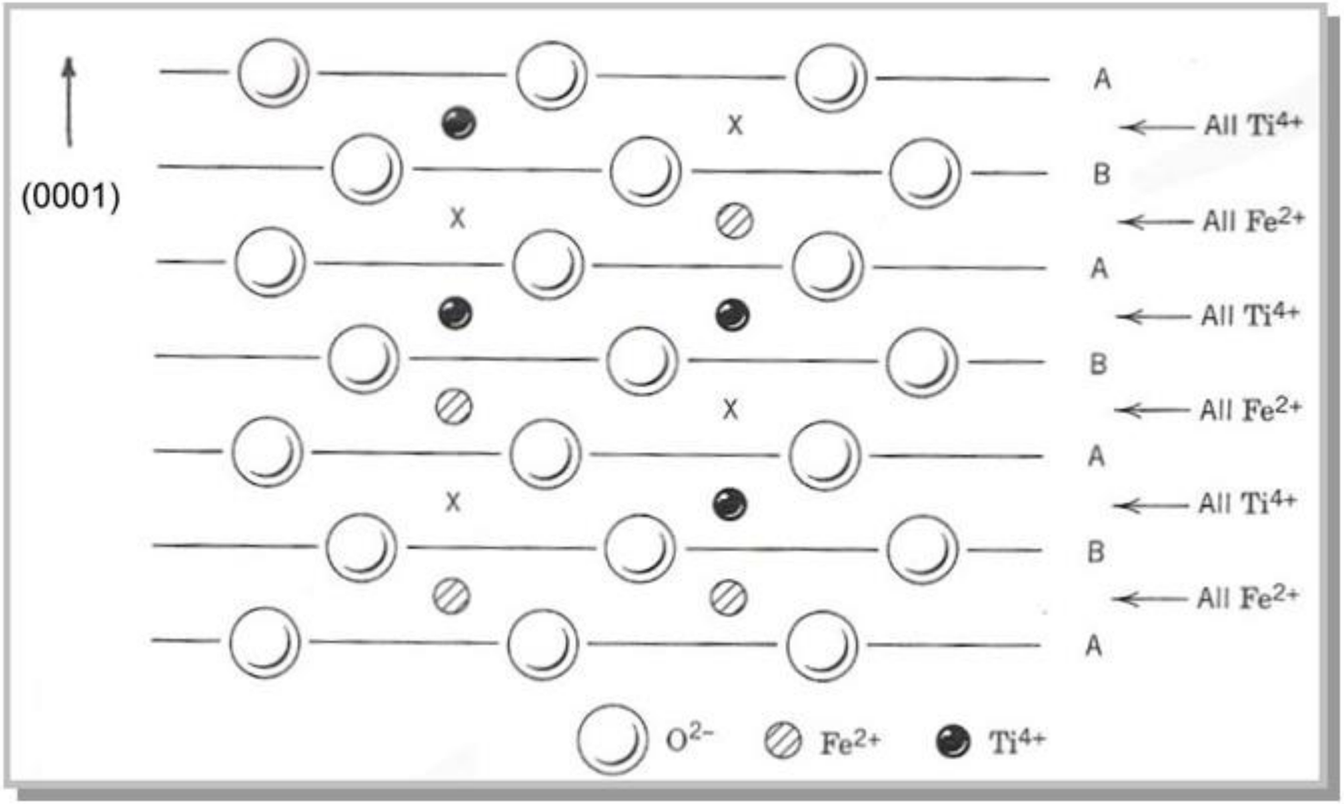


Figure 2.24 Ilmenite structure ({1120} plane) projection

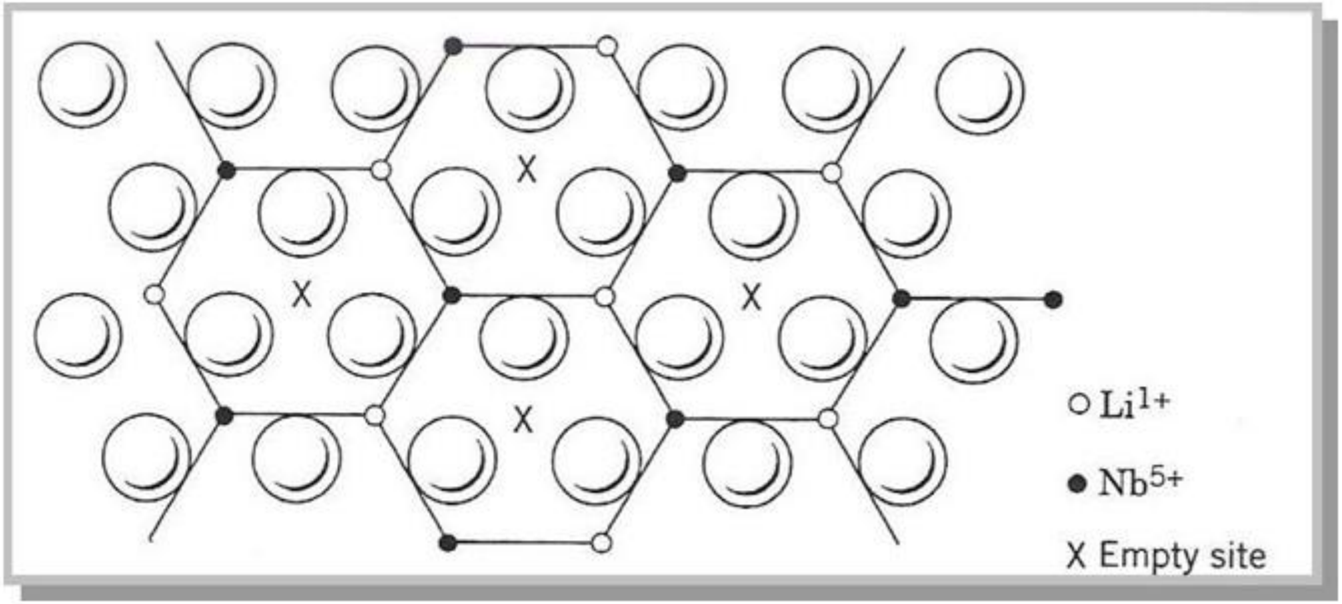


Figure 2.25 Basal plane of LiNbO3 structure, showing mixed Li, Nb occupancy.

Rutile: TiO_2

Rutile which is a polymorph of titanium oxide (the others are anatase and brookite), although tetragonal in symmetry (unit cell of rutile is tetragonal) is based on a quasi-HCP packing of oxygen atoms.

The octahedral interstices between close packed oxygen layers are half filled. Filling of the cations is on alternating diagonal rows and also in the direction perpendicular to the basal plane of HCP packing of anions. Thus, in the next layer the row above the filled raw in the previous layer is empty and vice versa.

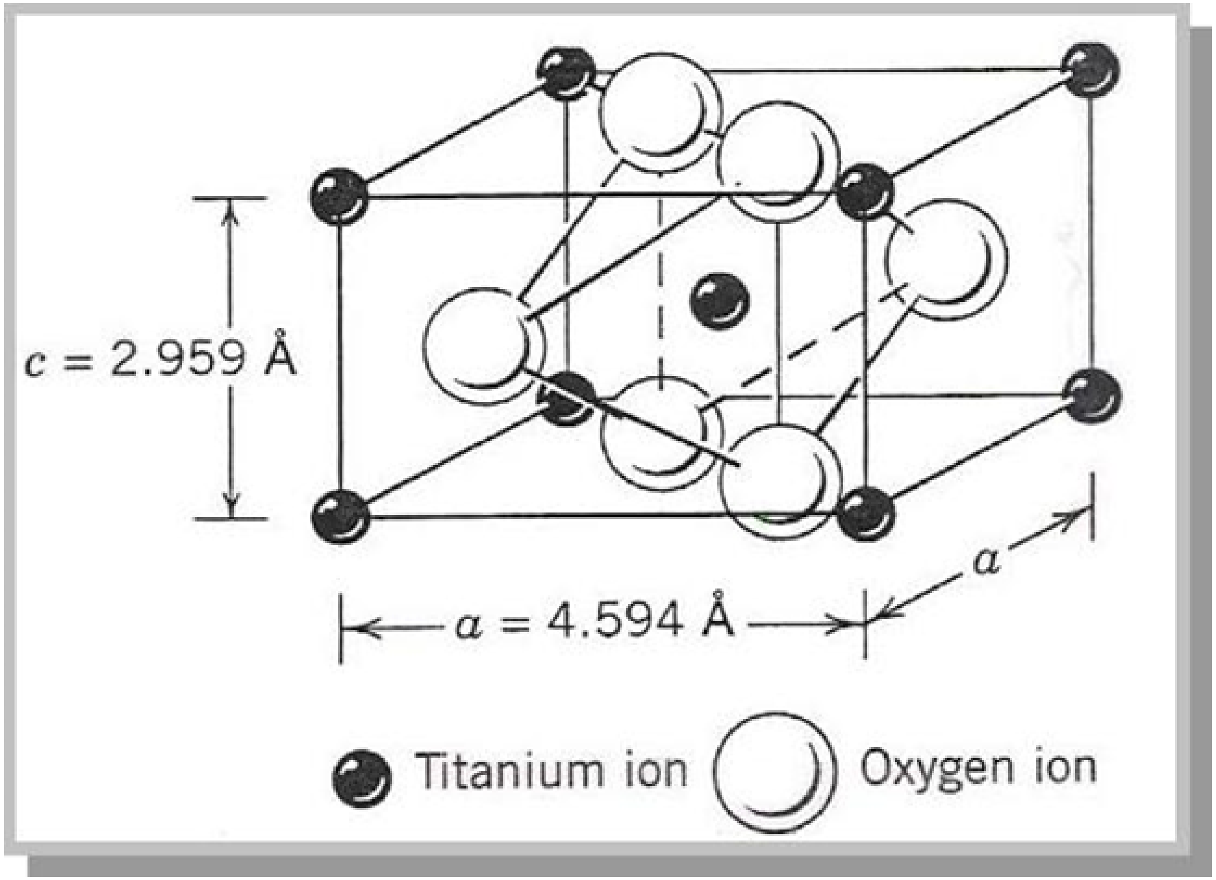


Figure 2.27 Unit cell of rutile structure

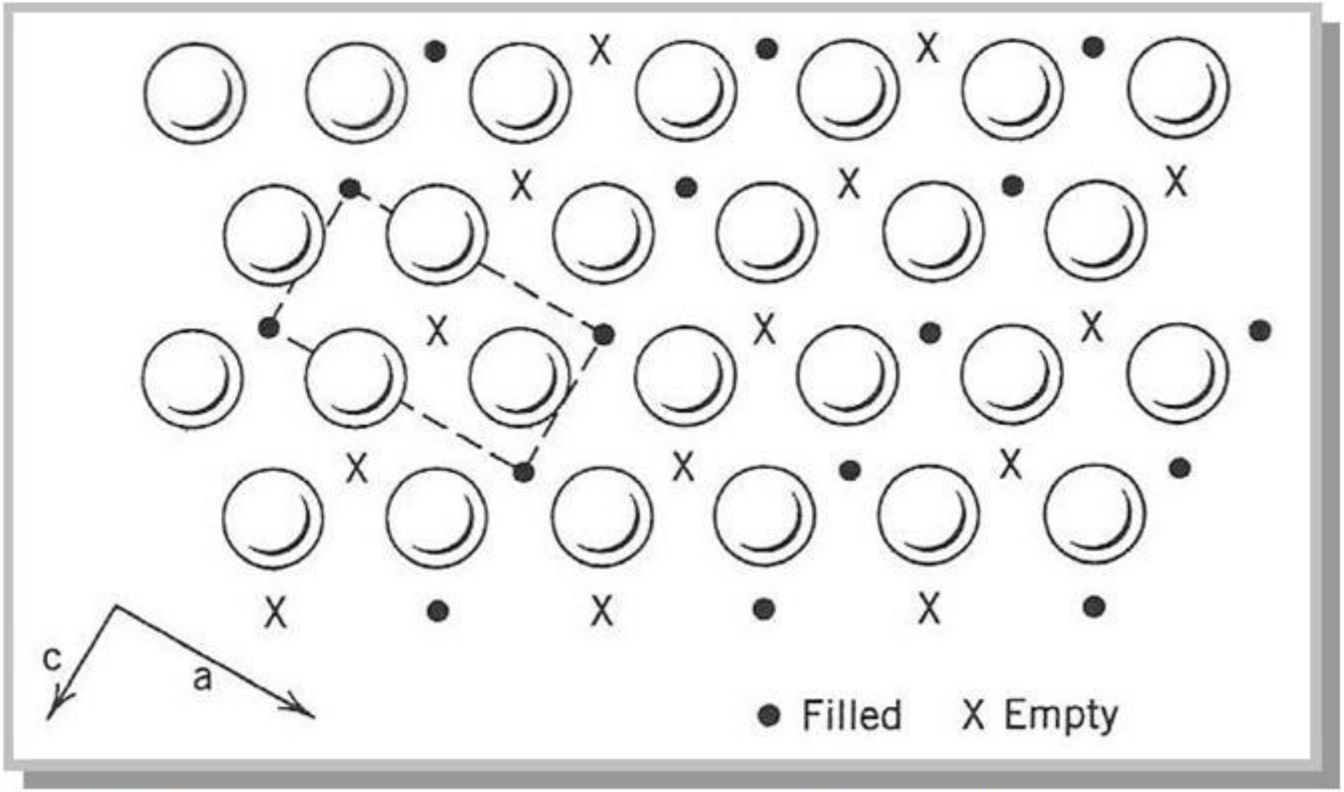


Figure 2.28 One-half filling of octahedral sites above a close-packed plane (rutile structure).

The tetragonal unit cell is outlined (in one view) with dashed lines. There are empty columns parallel to c-direction through which small ions can move fast. Rutile has high and highly anisotropic refractive index. So it has great scattering power.

PEROVSKITE Structure: ABO_3

In compounds with two different cations and an anion, for which the sizes of cations differ considerably, the large cation along with the anion can form a closed-packed structure; like in $CaTiO_3$ (perovskite), Where Ca^{+2} and O^{-2} form a closed-packed cubic structure, with the smaller cation (Ti^{+4}) in the octahedral interstitial site at the center of the cube. The small B cation (Ti^{+4}) has only 6 oxygen as nearest neighbors.

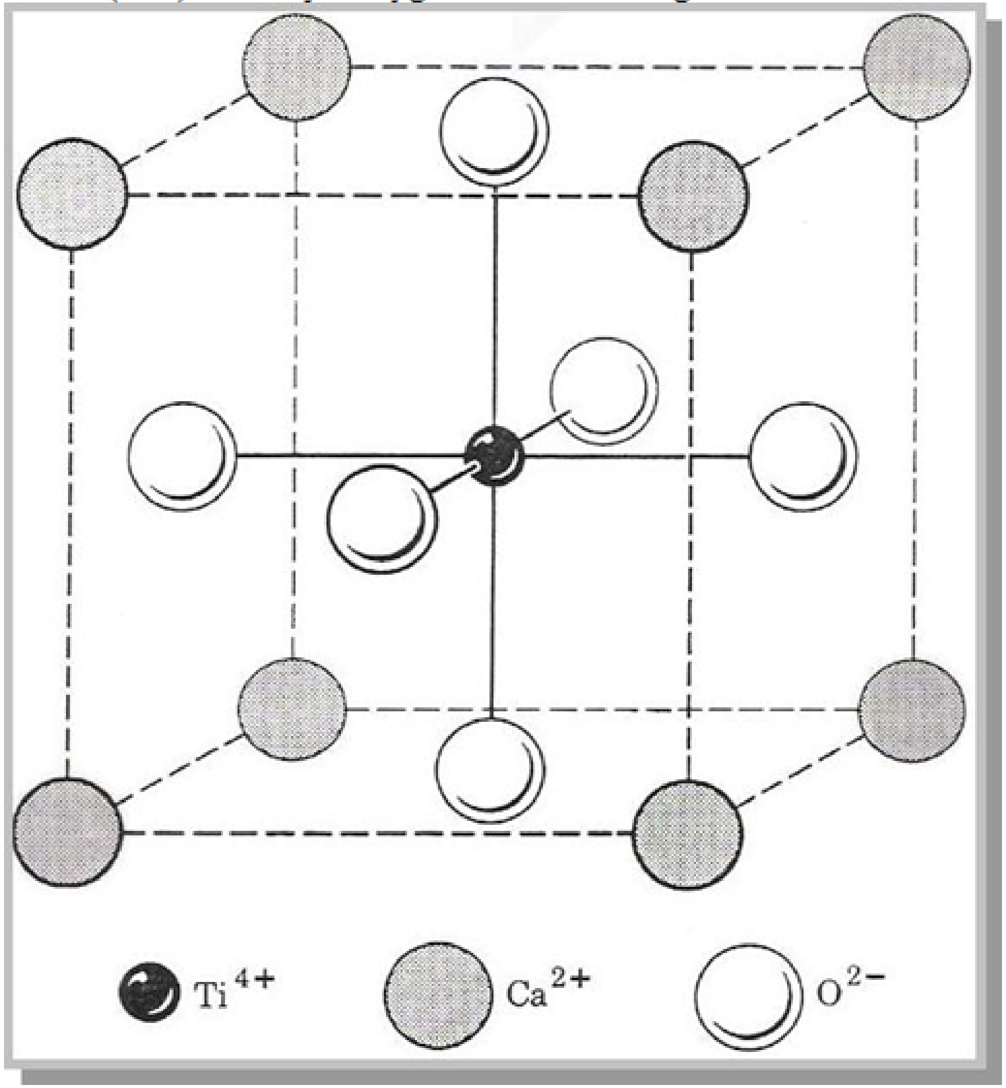


Figure 2.29 Perovskite Structure (idealized).

Many electroceramics of the titanate family crystallizes in this structure, $BaTiO_3$, $SrTiO_3$, $PbTiO_3$, $PbZrO_3$, Ba ZrO_3, $LaGaO_3$, $LaAlO_3$, $KNbO_3$, $YAlO_3$
In perovskite, each A-cation (Ca^{+2}) is surrounded by 12 oxygens. Each oxygen is coordinated with two Ti^{+4} and four Ca^{+2} cations.

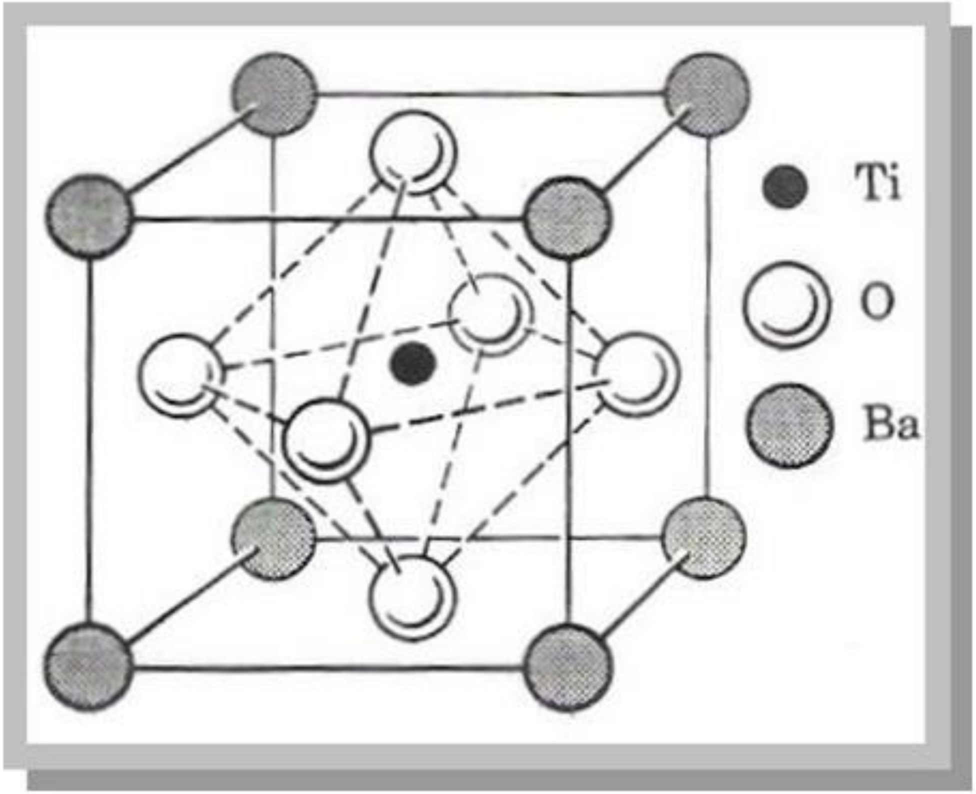


Figure 2.30 Ion positions in ideal cubic peroxide.

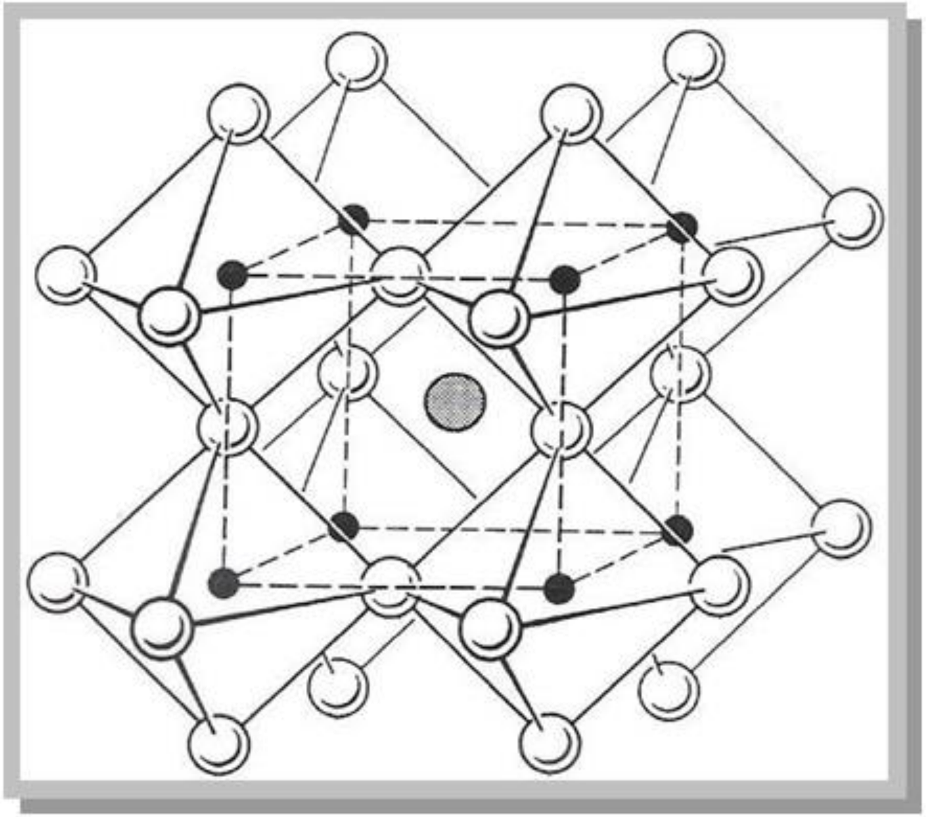


Figure 2.31 In perovskite, each A-cation (Ca^{+2}) is surrounded by 12 oxygens

Oxides with more complex stoichiometries can also crystallize in perovskite structure. The following combinations are possible:

$A^{+2}B^{+4}O_3$ → $BaTiO_3$, $PbZrO_3$
$A^{+3}B^{+3}O_3$ → $LaGaO_3$, $YAlO_3$
$A^{+2}(B^{+2}_{1/3}B^{+5}_{2/3})O_3$ → $Pb(Mg_{1/3}Nb_{2/3})O_3$
$A^{+2}(B^{+3}_{1/2}B^{+5}_{1/2})O_3$ → $Pb(Sc_{1/2}Ta_{1/2})O_3$

Spinel Structure: $A^{+2}B_2^{+3}O_4(AO.B_2.O_3)$

After mineral "spinel" $MgAl_2O_4$

B^{+3} cations (Al^{+3}) prefer octahedral sites and occupy half of all octahedral sites.

A^{+2} cations (Mg^{+2}) will occupy 1/8 of all tetrahedral sites.

The unit cell is based on FCC close packed oxygen sublattice, and contains 8 FCC oxygen subcells in a cubic arrangement.

A^{+2} in tetrahedral sites → 2/4 bond strength
B^{+3} in octahedral sites → 3/6 bond strength

Then oxygen is surrounded by 3 octahedral cation and 1 tetrahedral cation (Fig 2.41)

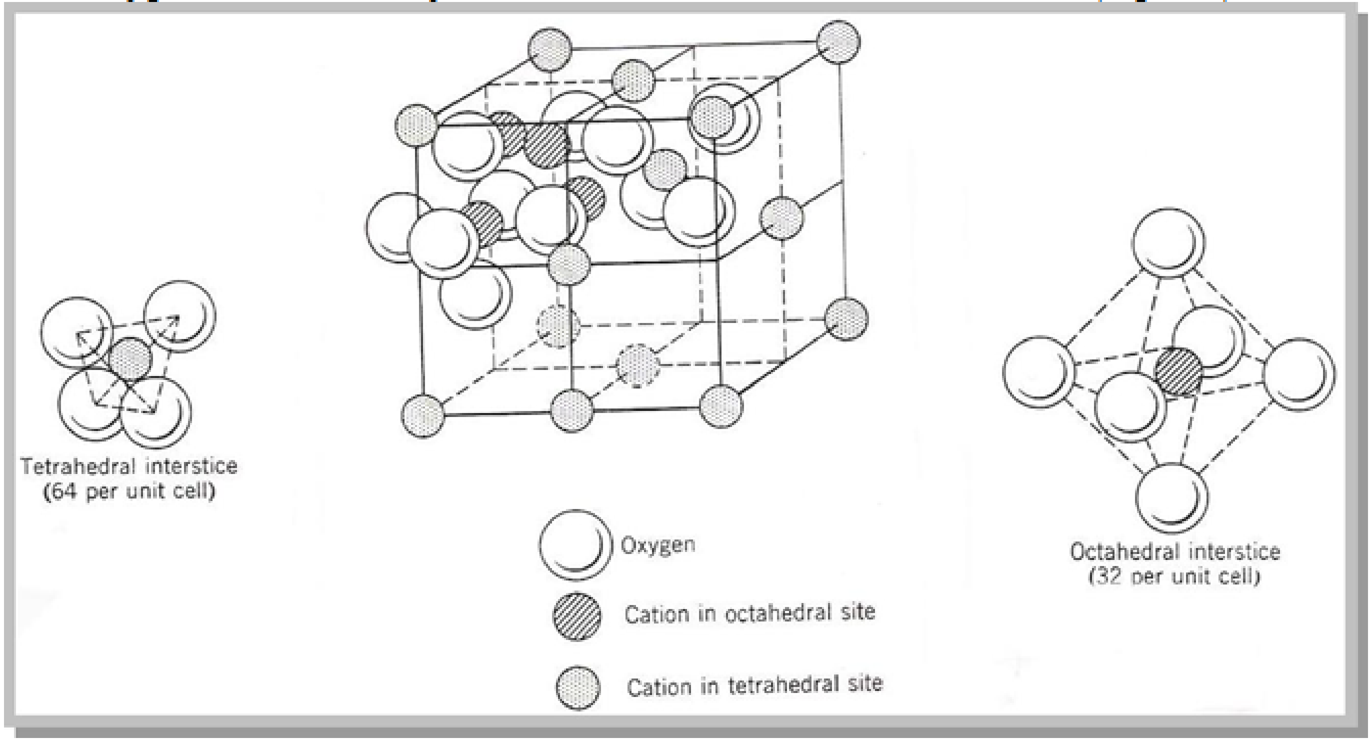
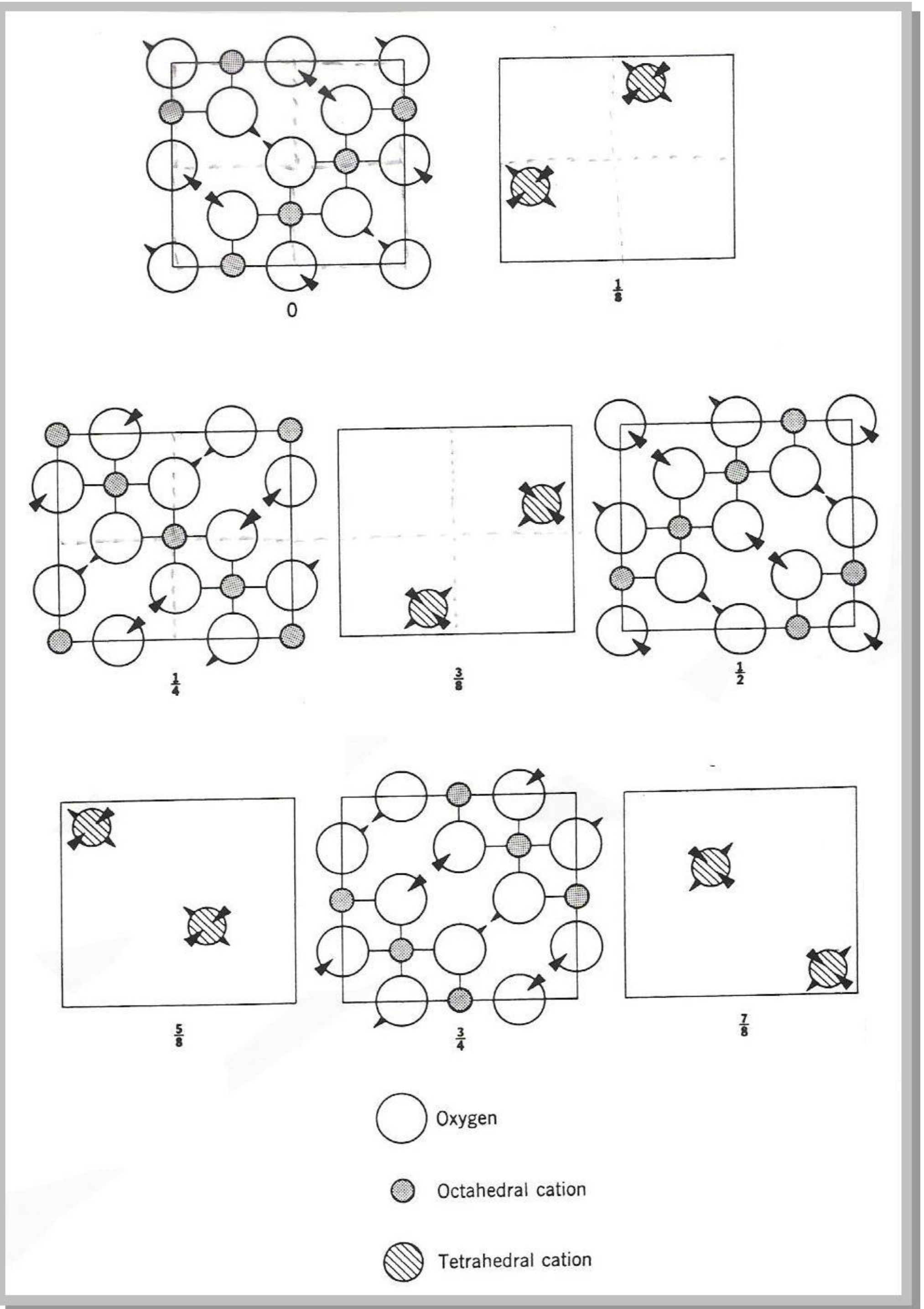


Figure 2.34 Atomic layers parallel to the (001) plane in spinel

Sequential layers parallel to (100) plane each slice is at a height of 1/8 a_o of the unit cell, which is made up of 8 oxygen FCC subcells.



The little arrow heads show bond directions from above and below of the slices. The distribution of cations in an inverse spinel is slightly different → $B(AB)O_4$.

In inverse spinel A^{+2} cations occupy ¼ of octahedral sites, half of B^{+3} cations occupy ¼ of the octahedral sites, the other half of the B^{+3} cations occupy the 1/8 of octahedral sites. The occupied sites are the same but the type of cations are changed.