



Structures & Properties of Ionic Solids

- **Ionic Radii and Ionic Solid structures**
- **Point defects:**
How are they different from those in metals?
- **Impurities:**
How are they accommodated in the lattice?
How do they affect properties?
- **Mechanical Properties:**
What special provisions/tests are made for ceramic materials?

1



Textbooks: Solid State Chemistry

1. Shriver, Atkins, *Inorganic Chemistry* (3rd ed, 1999)
W.H. Freeman and Company (Chs. 2, 18 ...).
2. A.R. West, *Basic Solid State Chemistry* (2nd ed. 1999)
Wiley, New York, 1999.
3. A. R. West, *Structural Inorganic Chemistry*, 5th ed.,
Oxford University Press, Oxford, 1984.
4. U. Muller, *Inorganic Structural Chemistry*, 2nd ed.,
Wiley, NY, 2006.

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The Ionic Model of Solids

The 'Ionic Model' (Goldschmidt')

Ions are essentially Charged, Incompressible, Non-Polarizable Spheres

More sophisticated model:

- a central hard, unperturbable core,
where most electron density is concentrated
- a soft, polarizable outer sphere,
which contains very little electron density

Pauling's Rules:

Goldschmidt's structural principles for ionic crystals were summarized by Pauling in a series of Rules.

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Pauling Rule 1: Coordination Polyhedra

**A coordination polyhedron of anions is formed around every cation (and vice-versa):
Only stable if cations are in contact with each neighbors.
(i.e., "Tight packing")**

Ionic crystals may thus be considered as sets of linked polyhedra.

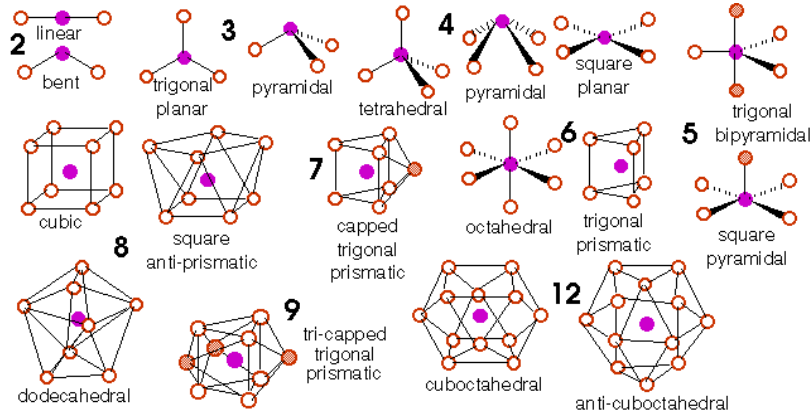
The cation-anion distance is regarded as the sum of the ionic radii.

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Pauling Rule 1: Coordination Polyhedra

Common Coordination Polyhedra:



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Pauling Rule 1: Coordination Polyhedra

The Coordination Number of the Cation will be Maximized subject to the criterion of Maintaining Cation-Anion Contact.

Determined by comparison of the ratio of the ionic radii, r_+/r_- with values derived from the **geometric contact criterion**:

The Radius Ratio Rules are correct **ONLY ~50% of the time!**

Limiting Radius Ratios - anions in the coordination polyhedron of cation are in contact with the cation and with each other {if cation were to shrink further (i.e. r_+/r_- decrease) cation-anion contact would be lost in contravention of Pauling's 1st Rule}.

Radius Ratio	Coordination no.	Binary (AB) Structure-type
$r_+/r_- = 1$	12	none known
$1 > r_+/r_- > 0.732$	8	CsCl
$0.732 > r_+/r_- > 0.414$	6	NaCl
$0.414 > r_+/r_- > 0.225$	4	ZnS

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Pauling Rule 2: Local Electroneutrality

Stable ionic structures preserve Local Electroneutrality.

Ions in a crystal are surrounded by ions of opposite charge so as not to produce large volumes of similar charge in the crystal - this *maximizes Madelung potential*

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Pauling Rule 3: Polyhedral Linking

The stability of structures with different types of polyhedral:

vertex-sharing > edge-sharing > face-sharing

1. effect is largest for cations with high charge and low coordination number
2. especially large when r^+/r^- approaches the lower limit of the polyhedral stability

Why?

Sharing edges/faces brings ions at the center of each polyhedron closer together, hence increasing **electrostatic repulsions**.

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Bonding in Ceramic Solids

% ionic character increases with difference in electronegativity;
but don't talk Pauling's % ionicity too literally!

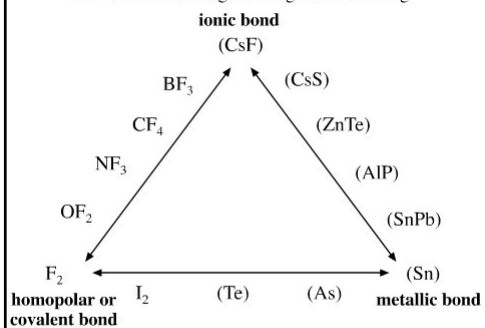
<i>Material</i>	<i>Percent Ionic Character</i>
CaF ₂	~ 89
MgO	~ 73
NaCl	~ 67
Al ₂ O ₃	~ 63
SiO ₂	~ 51
Si ₃ N ₄	~ 30
ZnS	~ 18
SiC	~ 12

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van Arkel Triangle: Bonding in Solids

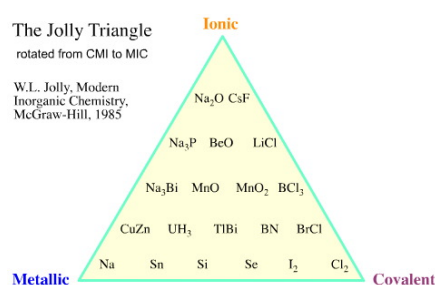
The van Arkel Triangular Diagram of Bonding



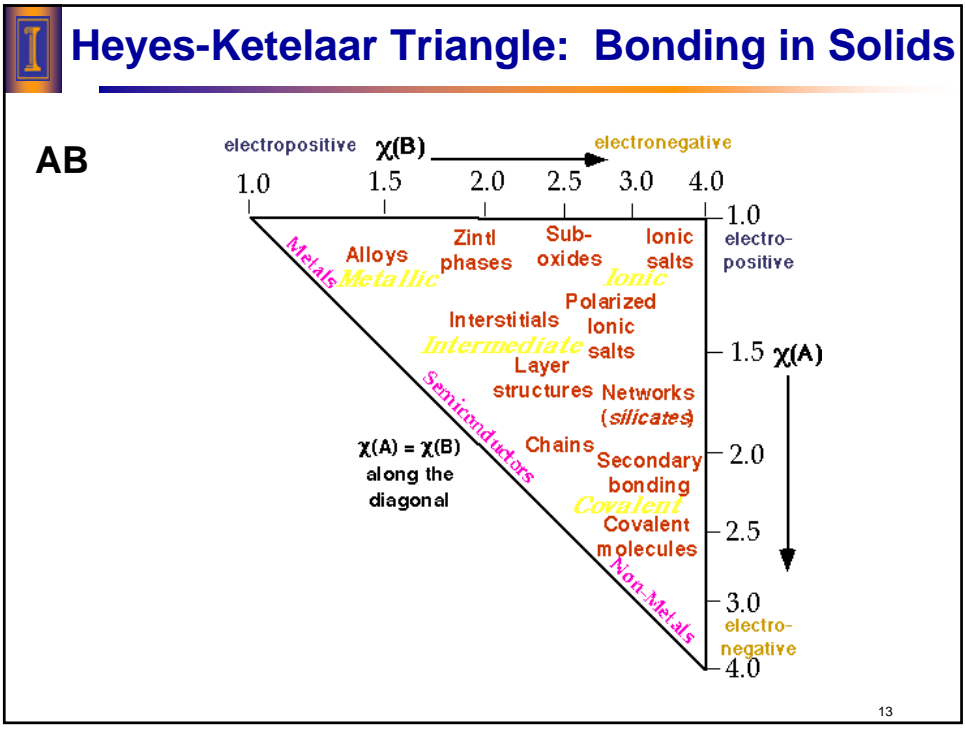
van Arkel, A.E., *Molecules and Crystals*, Butterworths, London, 1949, p205
first published in Dutch in 1941
(after Jensen *J.Chem.Educ.* (1995), 72, 395)

The Jolly Triangle
rotated from CMI to MIC

W.L. Jolly, *Modern Inorganic Chemistry*, McGraw-Hill, 1985



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Different types of atomic radii

(!! atoms can be treated as hard spheres !!)

elements or alloys

1 Metallic radius

element or compounds

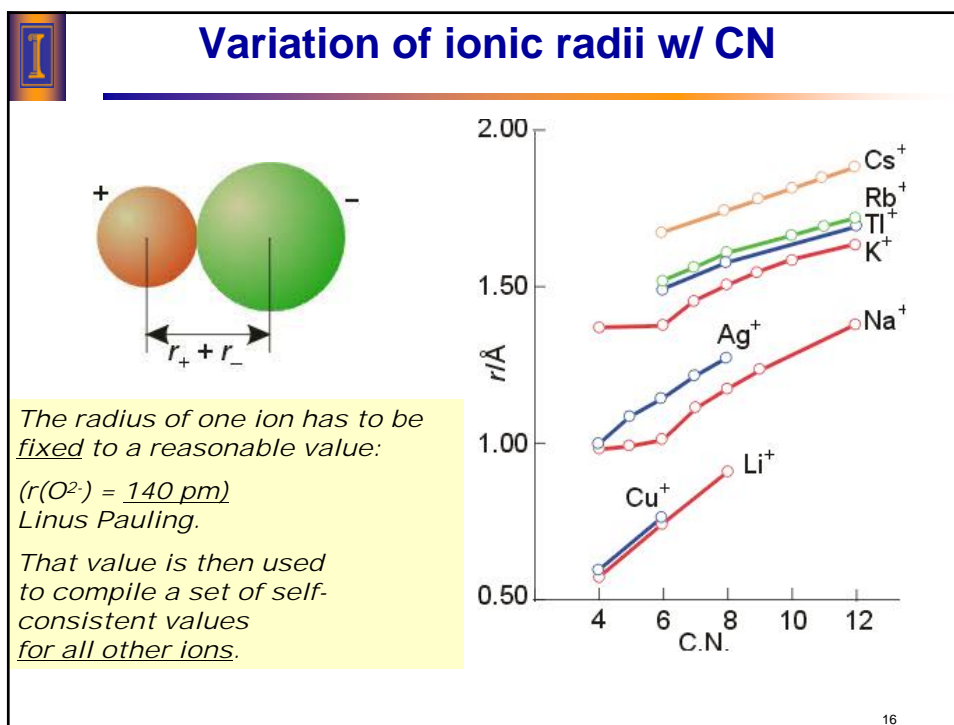
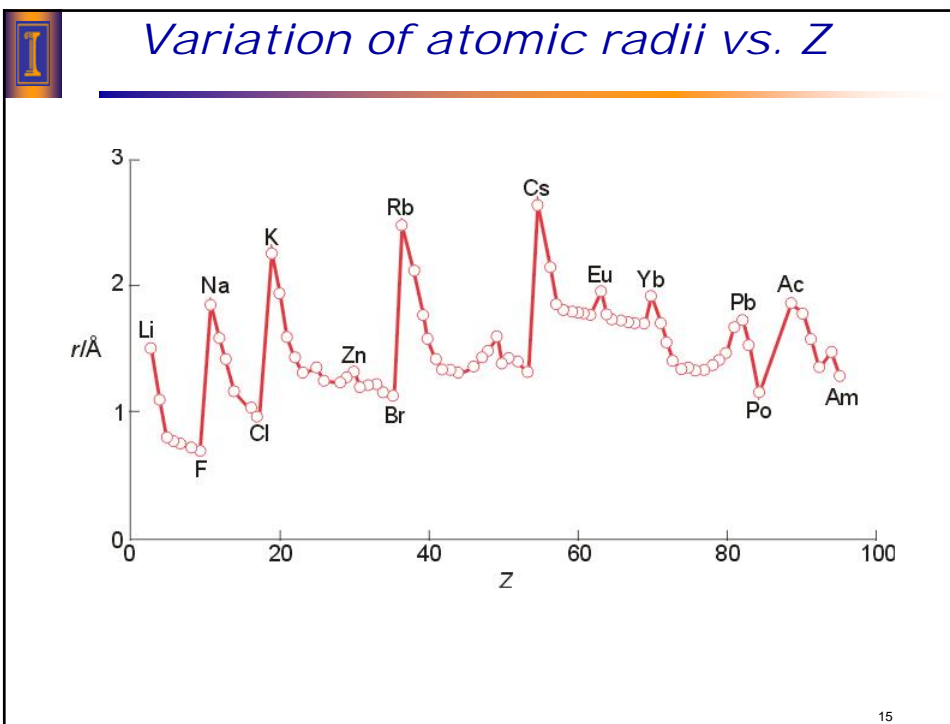
2 Covalent radius

ionic compounds

3 Ionic radius

Metals	Atomic radius = $d/2$ in element (metallic radius) Covalent radius = $d/2$ in single bond
Non-metals	Atomic radius = $d/2$ in element Covalent radius = $d/2$ in single bond

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Ionic Radii Defined

How are ionic radii determined?

A high-resolution X-ray diffraction map of the electron-density contours in sodium chloride. Numbers indicate the electron density (electrons/Å³) along each contour line. The "boundary" of each ion is defined as the minimum in electron density between the ions.

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General Trends For Ionic Radii

1. Ionic radii increase on going down a group. (Lanthanide contraction restricts the increase of heavy ions !!)
2. Radii of equal charge ions decrease across a period
3. Ionic radii increase with increasing coordination number (the higher its CN the bigger the ions seems to be !!)
4. The ionic radius of a given atom decreases with increasing charge ($r(\text{Fe}^{2+}) > r(\text{Fe}^{3+})$)
5. Cations are usually the smaller ions in a cation/anion combination (exceptions: $r(\text{Cs}^+) > r(\text{F}^-)$...!!!)
6. Frequently used for rationalization of structures:
"radius ratio" $r(\text{cation})/r(\text{anion}) (< 1)$

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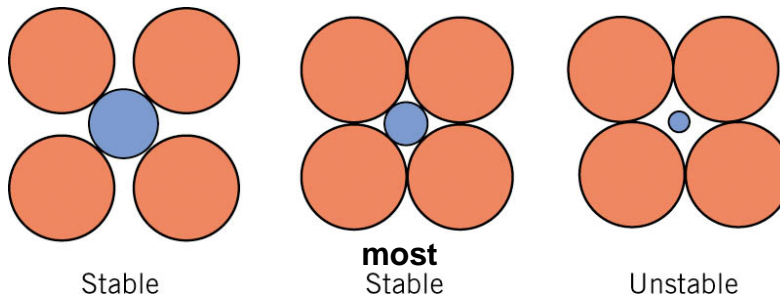
Ceramic Crystal Structures

Oxide structures

oxygen anions **much larger** than metal cations

close packed oxygen in a lattice (usually FCC)

cations in the holes of the oxygen lattice



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Ionic Radii

<i>Cation</i>	<i>Ionic Radius (nm)</i>	<i>Anion</i>	<i>Ionic Radius (nm)</i>
Al ³⁺	0.053	Br ⁻	0.196
Ba ²⁺	0.136	Cl ⁻	0.181
Ca ²⁺	0.100	F ⁻	0.133
Cs ⁺	0.170	I ⁻	0.220
Fe ²⁺	0.077	O ²⁻	0.140
Fe ³⁺	0.069	S ²⁻	0.184
K ⁺	0.138		
Mg ²⁺	0.072		
Mn ²⁺	0.067		
Na ⁺	0.102		
Ni ²⁺	0.069		
Si ⁴⁺	0.040		
Ti ⁴⁺	0.061		

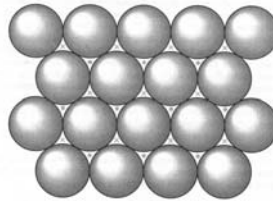
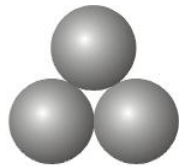
20



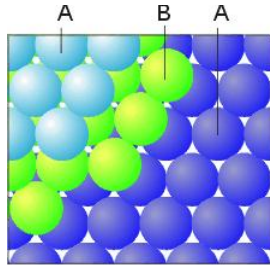
Principles of close packings of spheres

most important:

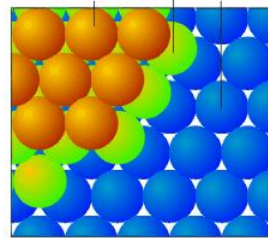
hexagonal close packing (hcp) and cubic close packing (ccp)



1 Close packing



(a)

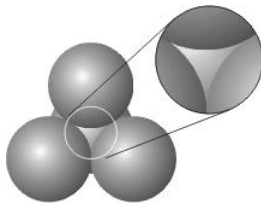


(b)

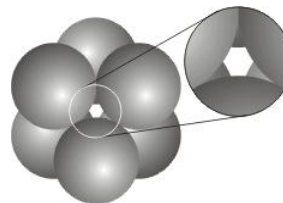
21



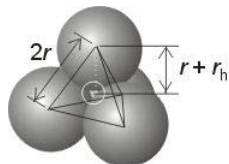
Holes in sphere packings



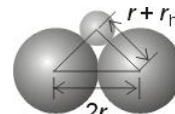
5 Tetrahedral hole



2 Octahedral hole



Calculation of
the relative size
of holes: r/r_h



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Structures with fully or partially filled octahedral and tetrahedral holes

<u>o/t</u>	fcc(ccp)	hcp
all <u>o</u> ct.	NaCl	NiAs
all <u>t</u> etr.	CaF ₂	(ReB ₂)
<u>o/t</u> (all)	(Li ₃ Bi)	(Na ₃ As)
½ <u>t</u>	sphalerite (ZnS)	wurtzite (ZnS)
(½ <u>o</u>	CdCl ₂	CdI ₂)

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Site Selection

Which sites will cations occupy?

1. Size of sites

does the cation fit in the site?

2. Stoichiometry

if all of one type of site is full, remaining cations have to go into other types of sites.

3. Bond Hybridization

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Coordination # and Ionic Radii

- Coordination # increases with $\frac{r_{\text{cation}}}{r_{\text{anion}}}$

How many anions (bigger) can be arranged around a cation (smaller)?

$\frac{r_{\text{cation}}}{r_{\text{anion}}}$	Coord #	
< 0.155	2	linear
0.155 - 0.225	3	triangular
0.225 - 0.414	4	T_D
0.414 - 0.732	6	O_H
0.732 - 1.000	8	cubic

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Cation Site Size

- Determine minimum $r_{\text{cation}}/r_{\text{anion}}$ for O_H site (C.N. = 6)

$$2r_{\text{anion}} + 2r_{\text{cation}} = \sqrt{2}a$$

$$a = 2r_{\text{anion}}$$

$$2r_{\text{anion}} + 2r_{\text{cation}} = 2\sqrt{2}r_{\text{anion}}$$

$$r_{\text{anion}} + r_{\text{cation}} = \sqrt{2}r_{\text{anion}} \quad r_{\text{cation}} = (\sqrt{2} - 1)r_{\text{anion}}$$

$$\frac{r_{\text{cation}}}{r_{\text{anion}}} = 0.414$$

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I Example: Predicting Structure of FeO

- On the basis of ionic radii, what crystal structure would you predict for FeO?

<table border="0"> <tr><td style="color: cyan;">Cation</td><td style="text-align: right;">Ionic radius (nm)</td></tr> <tr><td style="color: cyan;">Al³⁺</td><td style="text-align: right;">0.053</td></tr> <tr style="border: 1px solid red;"><td style="color: cyan;">Fe²⁺</td><td style="text-align: right;">0.077</td></tr> <tr><td style="color: cyan;">Fe³⁺</td><td style="text-align: right;">0.069</td></tr> <tr><td style="color: cyan;">Ca²⁺</td><td style="text-align: right;">0.100</td></tr> <tr><td colspan="2"> </td></tr> <tr><td style="color: green;">Anion</td><td></td></tr> <tr style="border: 1px solid red;"><td style="color: green;">O²⁻</td><td style="text-align: right;">0.140</td></tr> <tr><td style="color: green;">Cl⁻</td><td style="text-align: right;">0.181</td></tr> <tr><td style="color: green;">F⁻</td><td style="text-align: right;">0.133</td></tr> </table>	Cation	Ionic radius (nm)	Al ³⁺	0.053	Fe ²⁺	0.077	Fe ³⁺	0.069	Ca ²⁺	0.100			Anion		O ²⁻	0.140	Cl ⁻	0.181	F ⁻	0.133	<ul style="list-style-type: none"> Answer: $\frac{r_{\text{cation}}}{r_{\text{anion}}} = \frac{0.077}{0.140} = 0.550$ <p>based on this ratio, coord # = 6 structure = NaCl</p>
Cation	Ionic radius (nm)																				
Al ³⁺	0.053																				
Fe ²⁺	0.077																				
Fe ³⁺	0.069																				
Ca ²⁺	0.100																				
Anion																					
O ²⁻	0.140																				
Cl ⁻	0.181																				
F ⁻	0.133																				

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I Predicting Ionic Solid Structures

Correlation for cpds with AB structures

Rock Salt	58%
Zinc Blende	33%
Wurtzite	33%
Cesium Chloride	100%

Ex. ZnS $r_+/r_- = 0.52$

Zn²⁺ occupies T_d (not O_h) holes

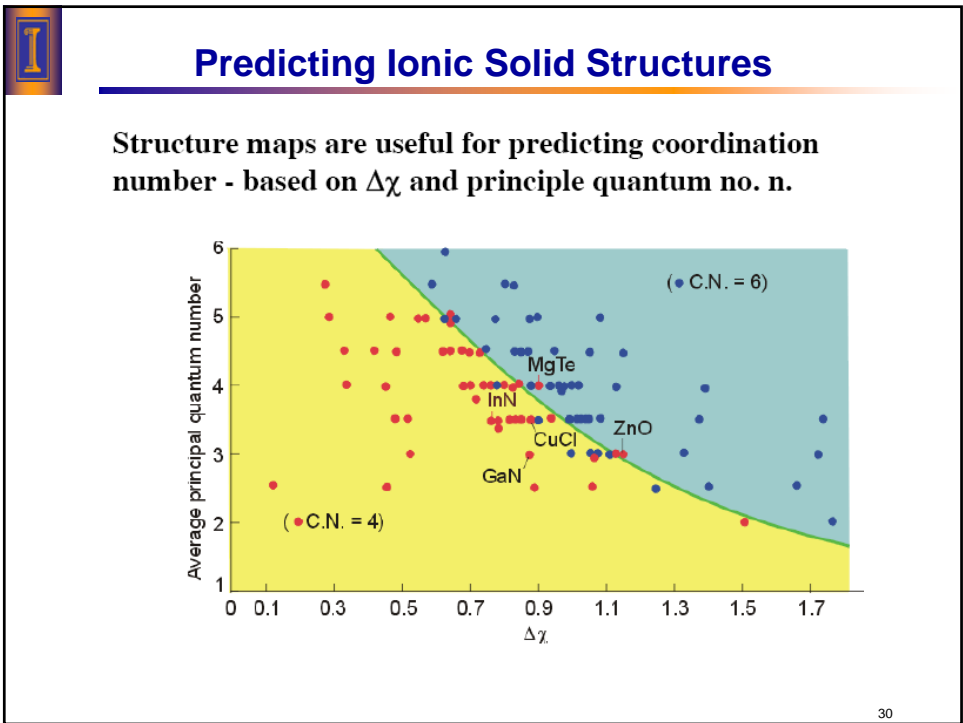
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Coordination Numbers

Structure Name	Structure Type	Anion Packing	Coordination Numbers		Examples
			Cation	Anion	
Rock salt (sodium chloride)	AX	FCC	6	6	NaCl, MgO, FeO
Cesium chloride	AX	Simple cubic	8	8	CsCl
Zinc blende (sphalerite)	AX	FCC	4	4	ZnS, SiC
Fluorite	AX ₂	Simple cubic	8	4	CaF ₂ , UO ₂ , ThO ₂
Perovskite	ABX ₃	FCC	12(A) 6(B)	6	BaTiO ₃ , SrZrO ₃ , SrSnO ₃
Spinel	AB ₂ X ₄	FCC	4(A) 6(B)	4	MgAl ₂ O ₄ , FeAl ₂ O ₄

Source: W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, *Introduction to Ceramics*, 2nd edition. Copyright © 1976 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.

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Site Selection II

2. Stoichiometry

If all of one type of site is full,
the remainder have to go into other types of sites.

Ex: FCC unit cell has 4 O_H and 8 T_D sites.

If for a specific ceramic each unit cell has 6 cations and the cation

4 in O_H

2 in T_D

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Site Selection III

3. Bond Hybridization – significant covalent bonding

the hybrid orbitals can have impact if significant covalent bond character

For example in SiC

$$X_{Si} = 1.8 \text{ and } X_C = 2.5$$

$$\% \text{ ionic character} \sim 100 \{1 - \exp[-0.25(X_{Si} - X_C)^2]\} = 11.5\%$$

- ca. 89% covalent bonding
- both Si and C prefer sp^3 hybridization
- Therefore in SiC get T_D sites

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Characteristic Structures of Solids I

The importance of the concepts of close packing of spheres in the crystal chemistry of elements and compounds:

holes in sphere packings

Rock salt: NaCl LiCl, KBr, AgCl, MgO, TiO, FeO, SnAs, UC ...

Fluorite: CaF₂ BaCl₂, K₂O, PbO₂ ...

Sphalerite: (zinc blende) ZnS CuCl, HgS, GaAs ...

Nickel arsenide: NiAs FeS, PtSn, CoS ...

Wurtzite: ZnS ZnO, MnS, SiC

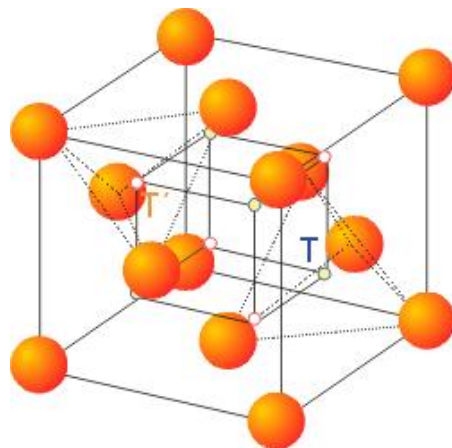
Further important structures of Solids

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Location and number of tetrahedral holes

in a fcc (ccp) unit cell

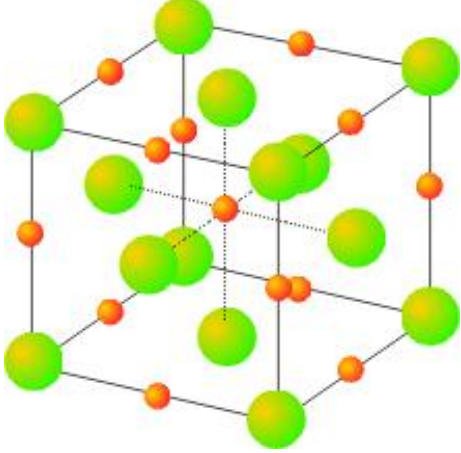


- $Z = 4$
(number of atoms in the unit cell)

- $N = 8$
(number of tetrahedral holes in the unit cell)

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I Location and number of octahedral holes in a fcc (ccp) unit cell



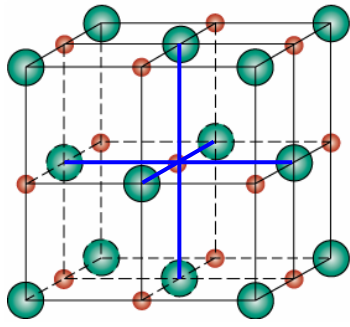
- $Z = 4$
(number of atoms in the unit cell)

- $N = 4$
(number of octahedral holes in the unit cell)

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I Rock Salt Structure

Same concepts can be applied to ionic solids in general.
 Example: NaCl (rock salt) structure



● Na⁺ $r_{\text{Na}} = 0.102 \text{ nm}$

● Cl⁻ $r_{\text{Cl}} = 0.181 \text{ nm}$

$r_{\text{Na}}/r_{\text{Cl}} = 0.564$

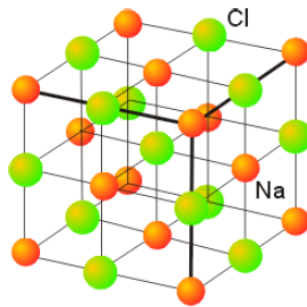
∴ cations prefer O_H sites

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Rock Salt Structure

Rock Salt: based on fcc array of anions. Cations occupy O_h holes, or the reverse.



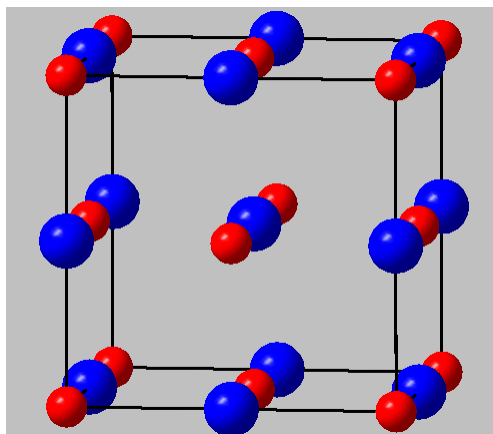
$$CN = 6 (6,6)$$

Ex. NaCl, LiCl, KBr, RbI, AgCl, AgBr, MgO, CaO, TiO, FeO, NiO, SnAs, UC, ScN

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Rock salt structure (NaCl)

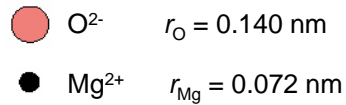
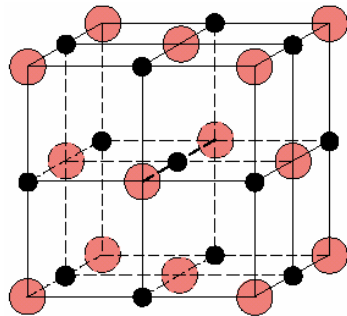


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MgO and FeO

MgO and FeO also have the NaCl structure



$$r_{Mg}/r_O = 0.514$$

\therefore cations prefer O_H sites

So each oxygen has 6 neighboring Mg^{2+}

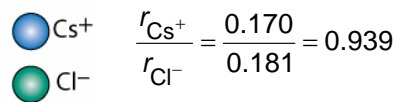
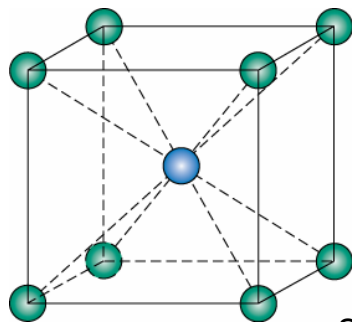
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AX Crystal Structures

AX-Type Crystal Structures include NaCl, CsCl, and zinc blende

Cesium Chloride structure:



\therefore cubic sites preferred

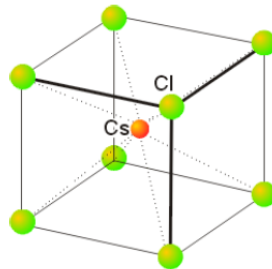
So each Cs^+ has 8 neighboring Cl^-

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AX Crystal Structures

Cesium chloride: cubic unit cell with cesium cation in cubic 'hole',
(or vice versa)



CN = 8 (8,8)

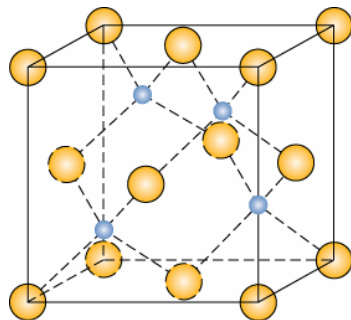
Ex: CsCl, CaS, TlSb, CsCN, CuZn

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AX Crystal Structures

Zinc Blende structure



● Zn²⁺ ● S²⁻

$$\frac{r_{\text{Zn}^{2+}}}{r_{\text{O}^{2-}}} = \frac{0.074}{0.140} = 0.529 \Rightarrow O_H??$$

- Size arguments predict Zn²⁺ in O_H sites,
- In observed structure Zn²⁺ in T_D sites
- Why is Zn²⁺ in T_D sites?

bonding hybridization of zinc favors T_D s

So each Zn²⁺ has 4 neighboring O²⁻

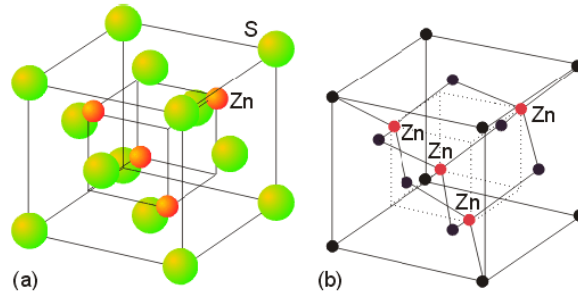
Ex: ZnO, ZnS, SiC

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AX Crystal Structures

Sphalerite (zinc-blende): expanded fcc anion lattice - Zn^{2+} occupies half of the T_d holes

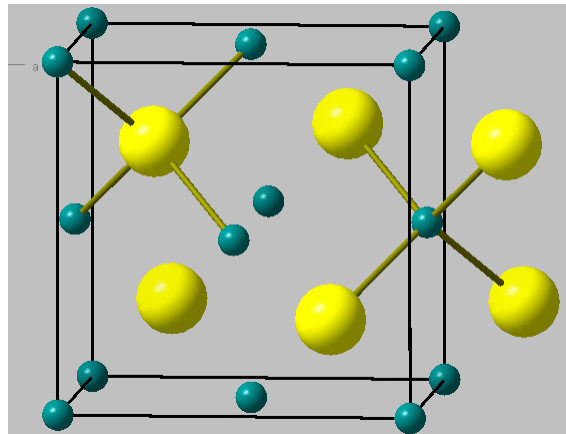


CN = 4 (4,4)

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Sphalerite (zincblende)

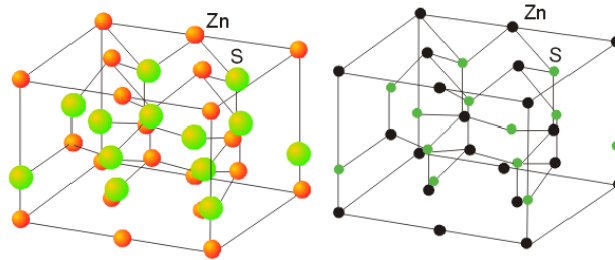


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Wurtzite type

Wurtzite: another polymorph of ZnS - based on a hcp lattice. Again Zn^{2+} cations occupy half of the T_d holes.



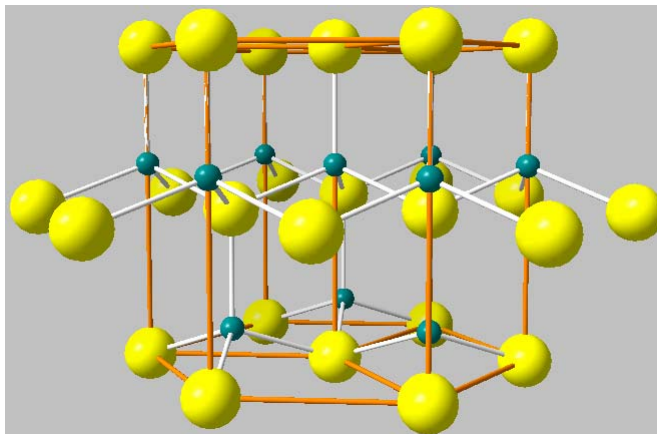
CN: (4,4)

Ex: ZnS, ZnO, BeO, MnS, AgI, AlN, SiC, NH₄F

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Wurtzite type

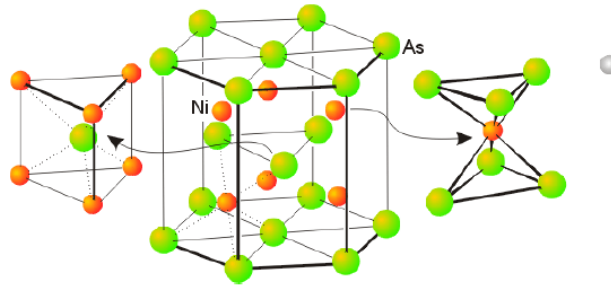


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NiAs - type

Nickel arsenide: hcp array of anions with Ni^{3+} occupying octahedral Holes - typical of MX compounds containing polarizable (soft) cations and anions.

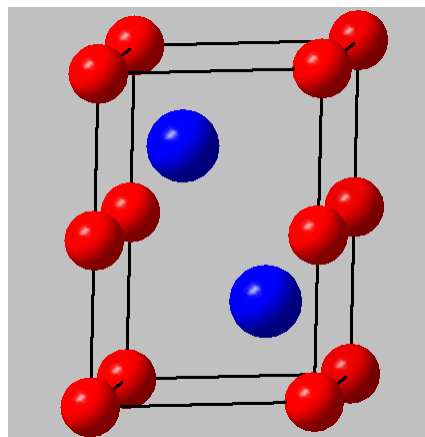


CN (6,6)

Ex. NiAs, NiS, FeS, PtSn, CoS



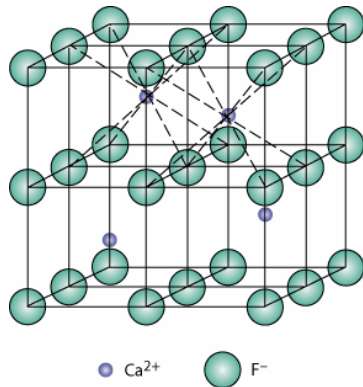
NiAs - type





AX₂ Crystal Structures

Fluorite structure



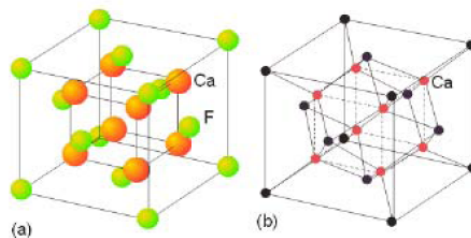
- Calcium Fluorite (CaF₂)
- cations in cubic sites
- UO₂, ThO₂, ZrO₂, CeO₂
- antifluorite structure – cations and anions reversed

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AX₂ Crystal Structures

Fluorite: named for CaF₂ structure. Expanded fcc array of Ca²⁺ ions
With F⁻ anions in all 2N T_d holes. Ex: CaF₂, UO₂, BaCl₂, HgF₂, PbO₂



CN (8,4) because there are 2x as many anions as cations

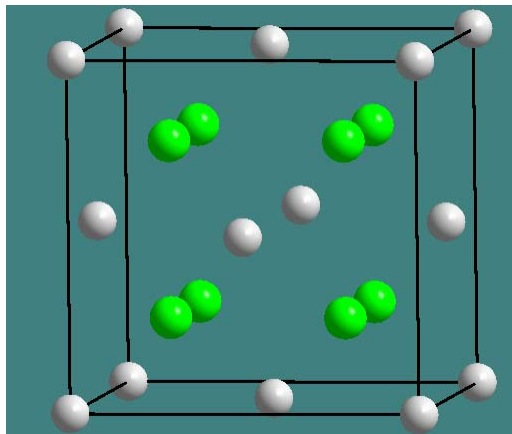
Antifluorite: simply the opposite with 2x as many cations as anions

Ex: K₂O, K₂S, Li₂O, Na₂O, Na₂Se, Na₂S

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Fluorite structure (CaF₂)

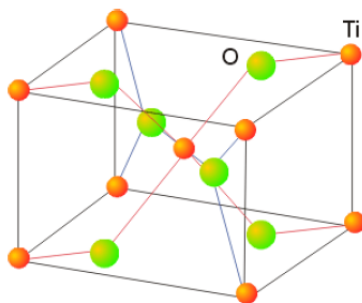


51



The rutile structure: TiO₂

Rutile: named for a mineral form of TiO₂. Hcp array of oxygen anions with Ti⁴⁺ occupying half of the O_h holes.



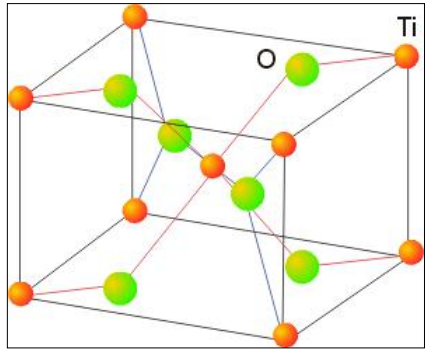
CN (6,3)

Ex. TiO₂, MnO₂, SnO₂, WO₂, MgF₂, NiF₂

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The rutile structure: TiO_2



TiO_6 - octahedra

OTi_3 - trigonal planar

(alternative to the Fluorite structure for highly charged smaller cations, e.g. Ti^{4+})

Rutile: ceramic pigment (white color)

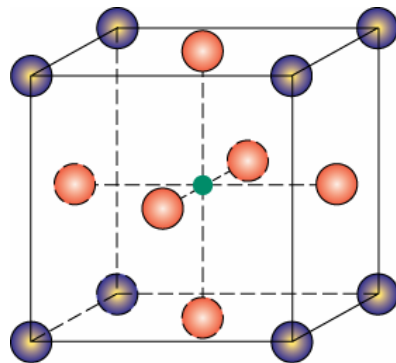
53



ABX_3 Crystal Structures

- Perovskite

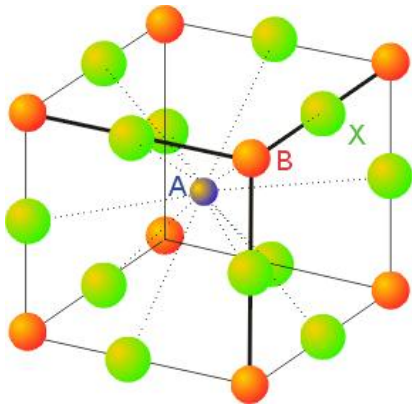
Ex: complex oxide



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The perovskite structure CaTiO_3



- TiO_6 - octahedra

- CaO_{12} - cuboctahedra

(Ca^{2+} and O^{2-} form a cubic close packing)

→ preferred basis structure of piezoelectric, ferroelectric and superconducting materials

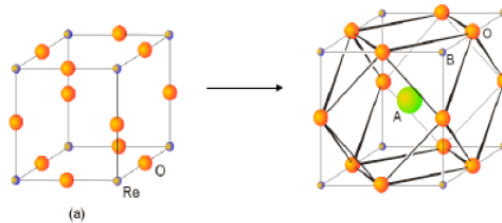
55



The perovskite structure CaTiO_3

Perovskite: named for the mineral CaTiO_3 . Prototypical structure of Many ABX_3 solids. X is commonly an oxide or fluoride anion. A is a large cation (12 coordinate) B is a smaller cation (CN 6). Ideally Structure is cubic.

Take unit cell of ReO_3 and plop a large cation in the middle



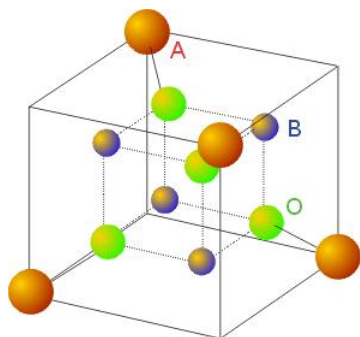
Ex. CaTiO_3 , BaTiO_3 , SrTiO_3

Materials with perovskite structure often exhibit interesting electrical properties (e.g. piezoelectricity, ferroelectricity, high temp. superconductivity).

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The spinell structure: $MgAl_2O_4$



fcc array of O^{2-} ions, Mg^{2+} occupies 1/8 of the tetrahedral and Al^{3+} 1/2 of the octahedral holes

→ *normal spinell:*
 AB_2O_4

→ *inverse spinell:*
 $B[AB]O_4$ (Fe_3O_4):
 $Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$

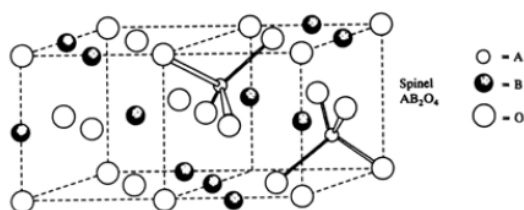
→ *basis structure for several magnetic materials*

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The spinell structure: $MgAl_2O_4$

Spinel: named after the mineral $MgAl_2O_4$. General formula is AB_2O_4 . Consists of fcc array of oxide anions. A cations occupy 1/8 of T_d holes. B cations occupy half the O_h holes.



Common structure of mixed-valent, d-block oxides - e.g. Fe_3O_4 , Co_3O_4 , Mn_3O_4 . Also have inverse spinels: $B[AB]O_4$.

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Summary

- Ionic Solids structures are based on:
charge neutrality
maximizing # of nearest oppositely charged neighbors.
- Limited family of common ionic structures.
- Structures may be predicted from the ratio of the cation and anion radii.