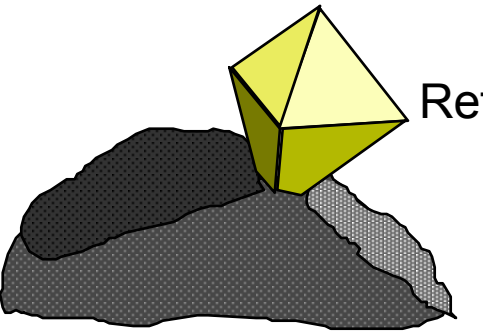
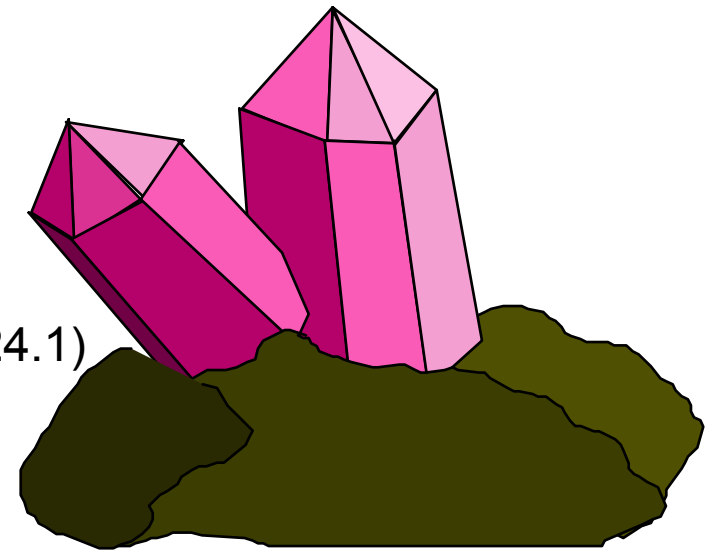
Crystals

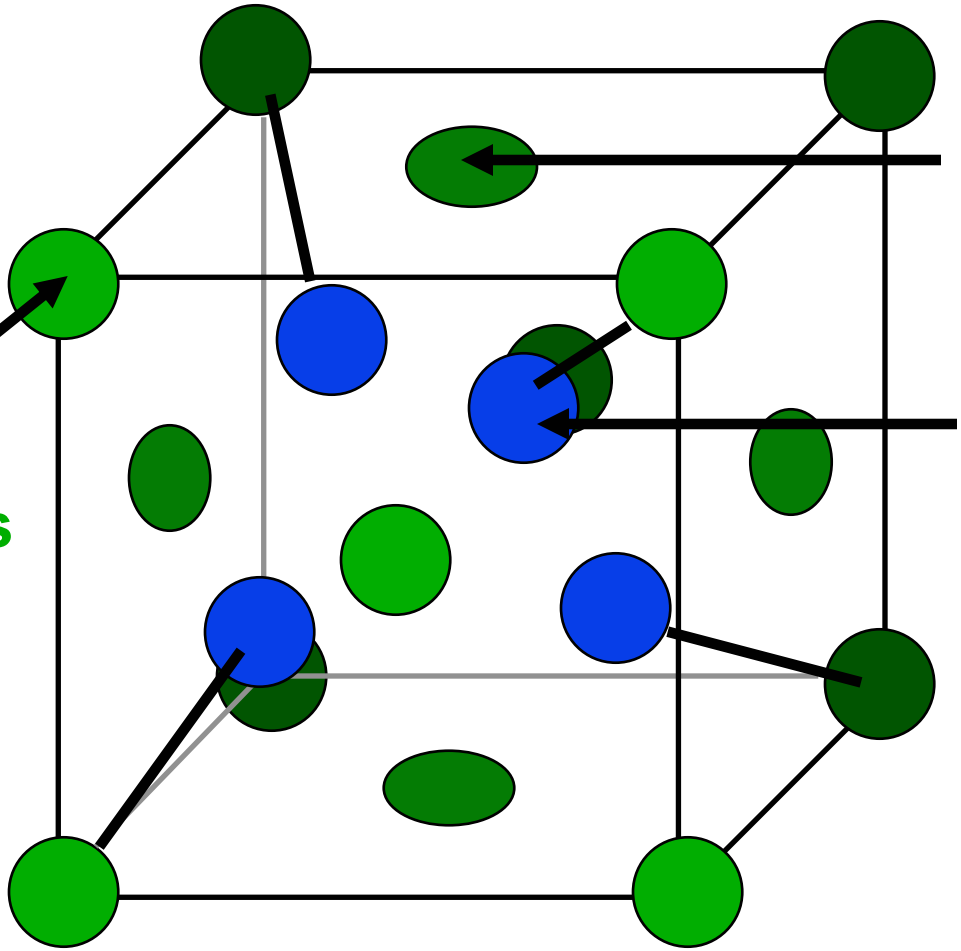
Part 2



References: Gray: Chapter 6
OGN: Chapter 19 and (24.1)



Stoichiometry of Zinc Blende



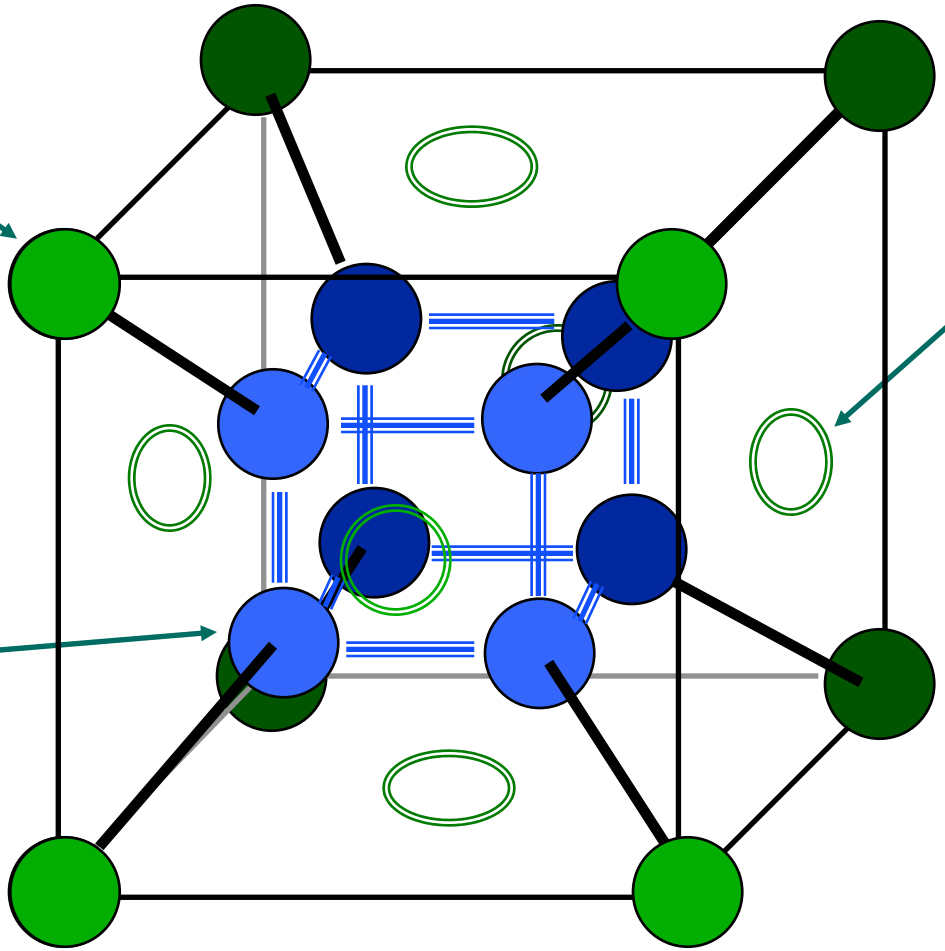
Face Atoms
(6 * 1/2 = 3)

T_d Holes
(4 * 1 = 4)

Corner Atoms
(8 * 1/8 = 1)

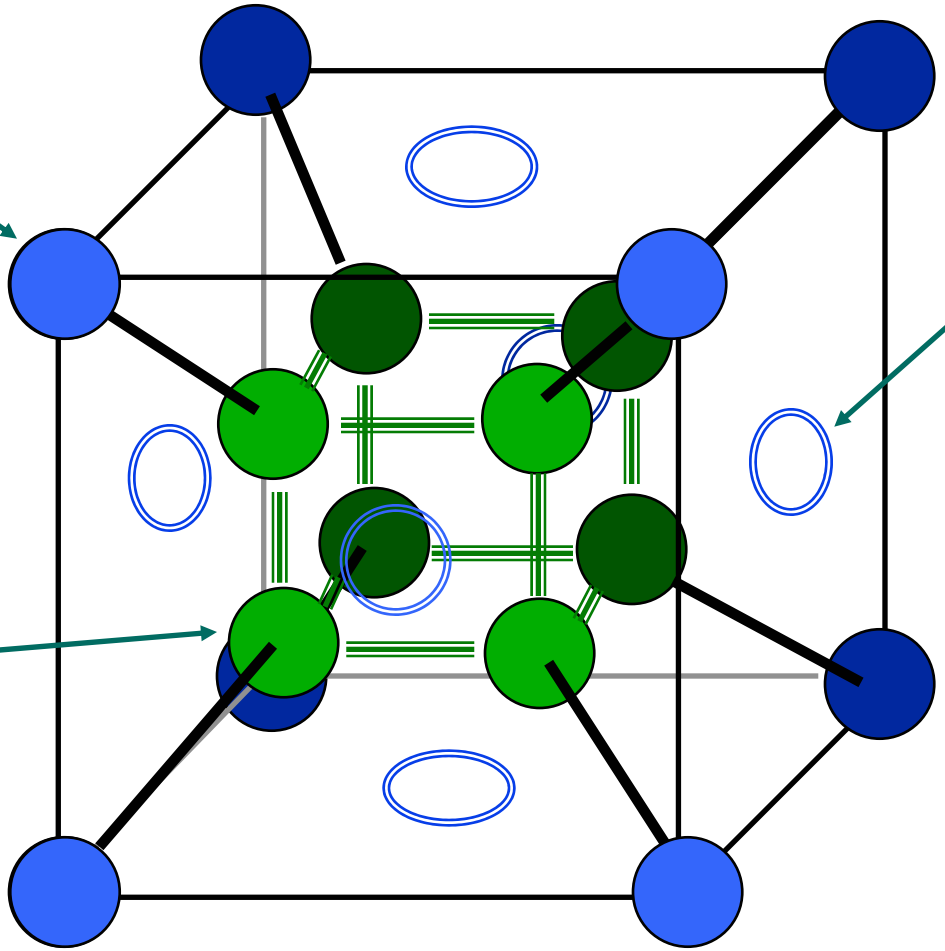
4 Lattice Atoms: 4 Tetrahedral Holes
1:1 Stoichiometry (GaAs, InP, CdS, ZnS)

Stoichiometry of Anti-Fluorite



4 Lattice Anions: 8 Tetrahedral Cations
1:2 Stoichiometry (Li_2O, Na_2O, Li_2S)

Stoichiometry of Fluorite



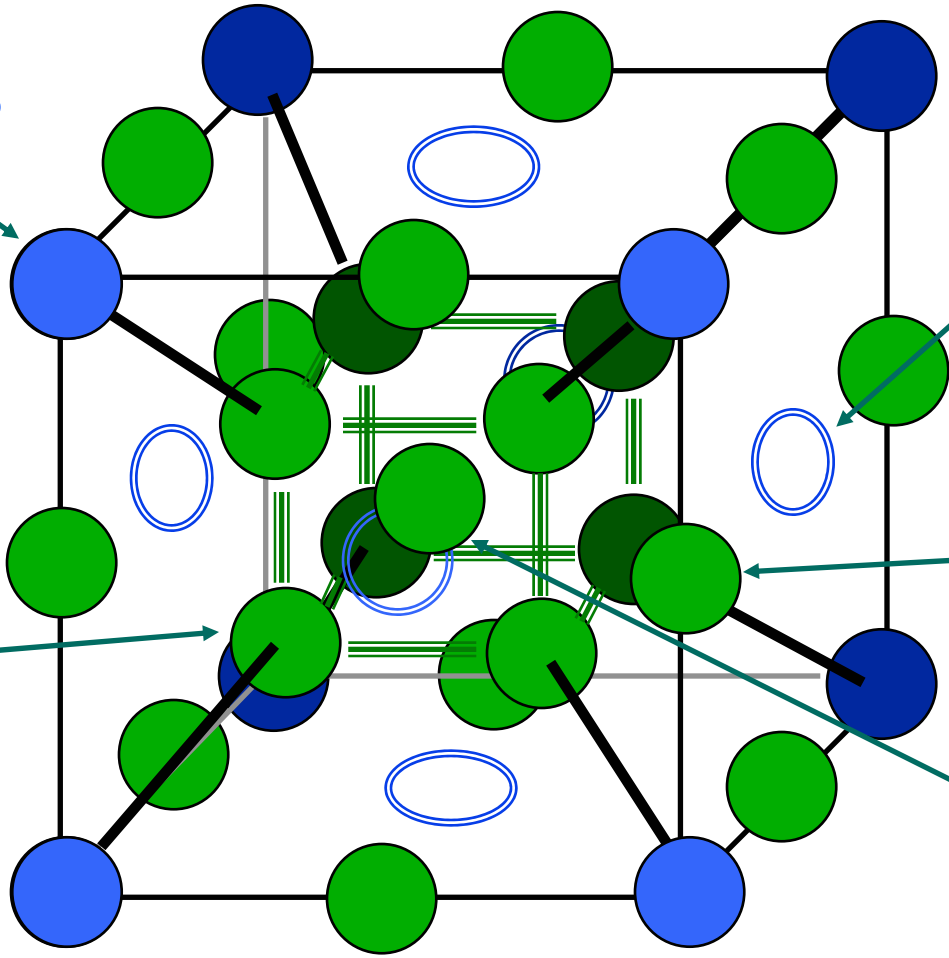
Corner Atoms
(8 * 1/8 = 1)

Face Atoms
(6 * 1/2 = 3)

T_d Holes
(8 * 1 = 8)

4 Lattice Cations: 8 Tetrahedral Anions
1:2 Stoichiometry (CaF_2, $SrCl_2$, HgF_2)

Stoichiometry of Li_3B



Corner Atoms
(8 * 1/8 = 1)

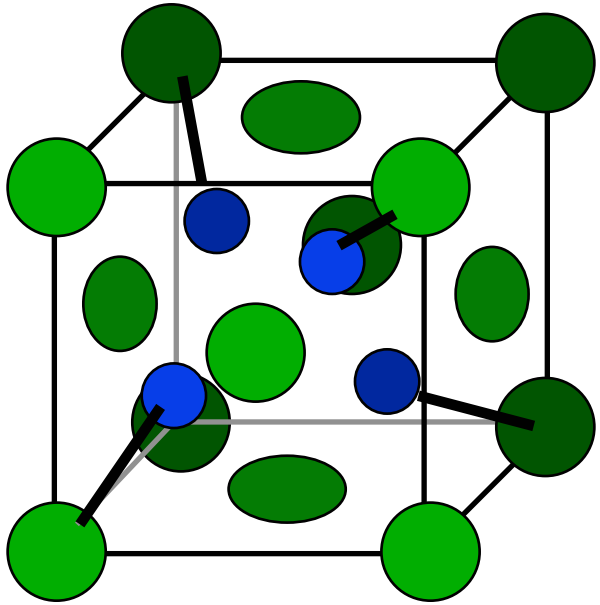
Face Atoms
(6 * 1/2 = 3)

O_h Holes
(12 /4 = 3)

T_d Holes
(8 * 1 = 8)

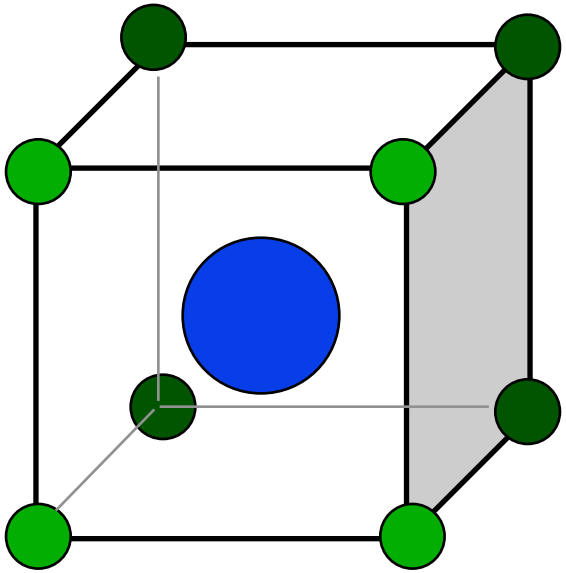
O_h Hole
(1)

4 Lattice Anions: 8 Tetrahedral Cations + 4 Octahedral Cations
1:3 Stoichiometry (Li_3B)

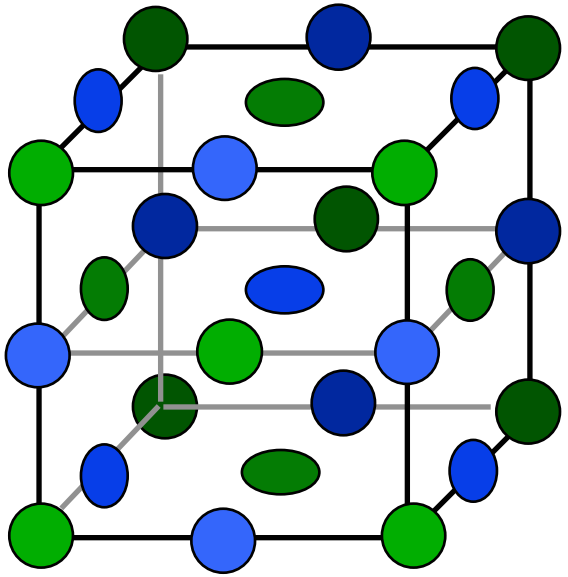


ZnS
(Smallest
Cation/Anion)

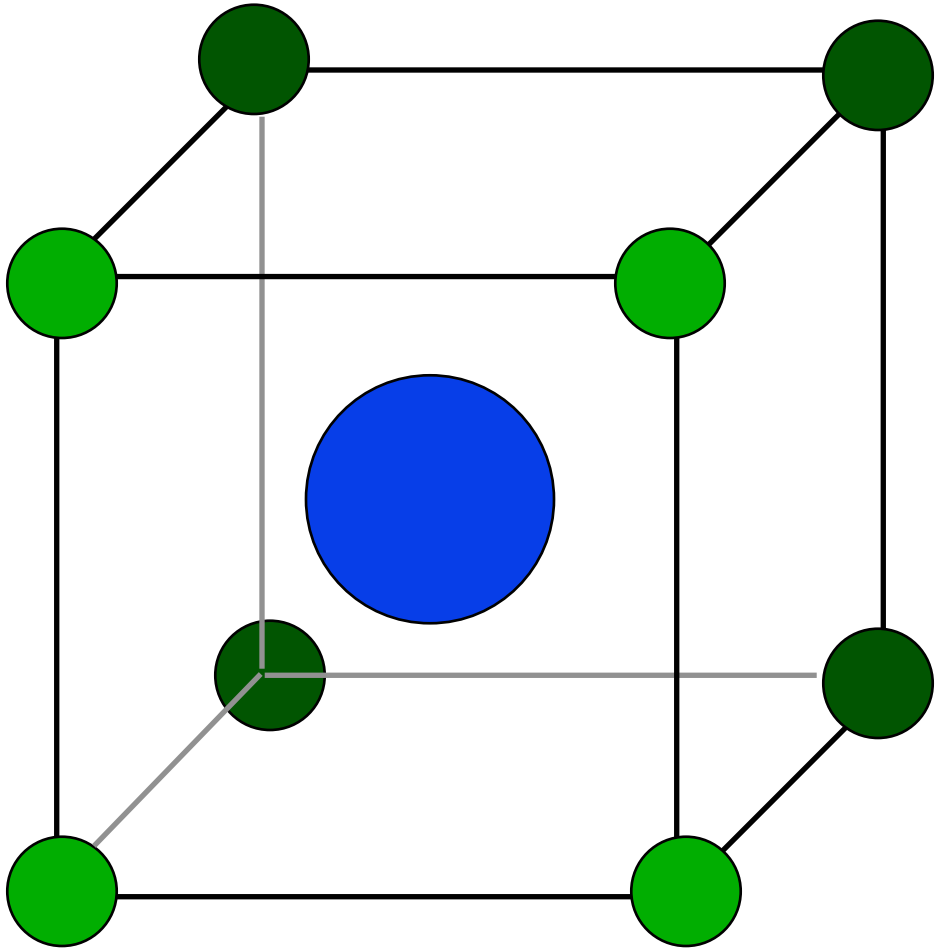
CsCl
(Biggest Cation/Anion)



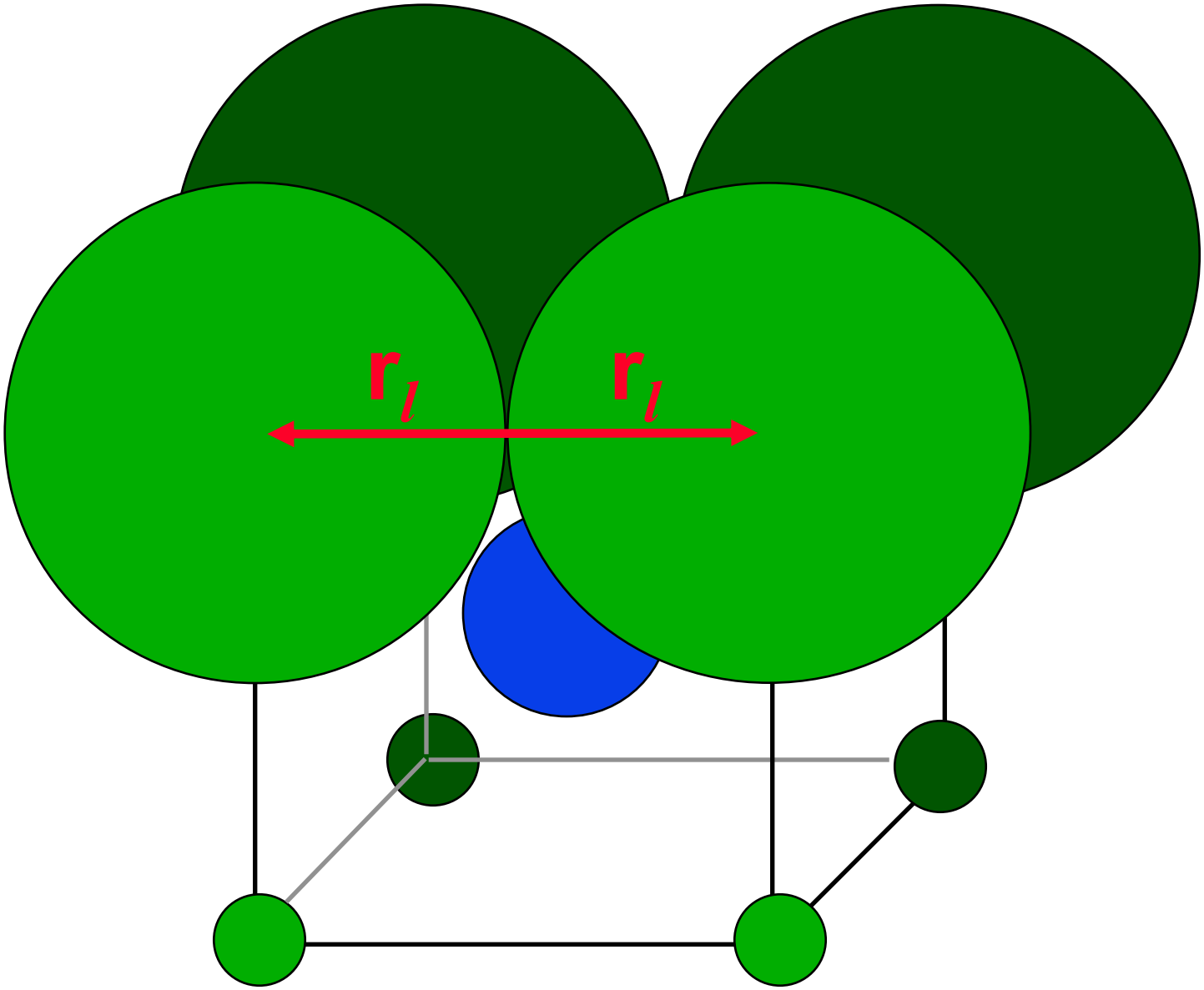
NaCl
(Intermediate Cation/Anion)



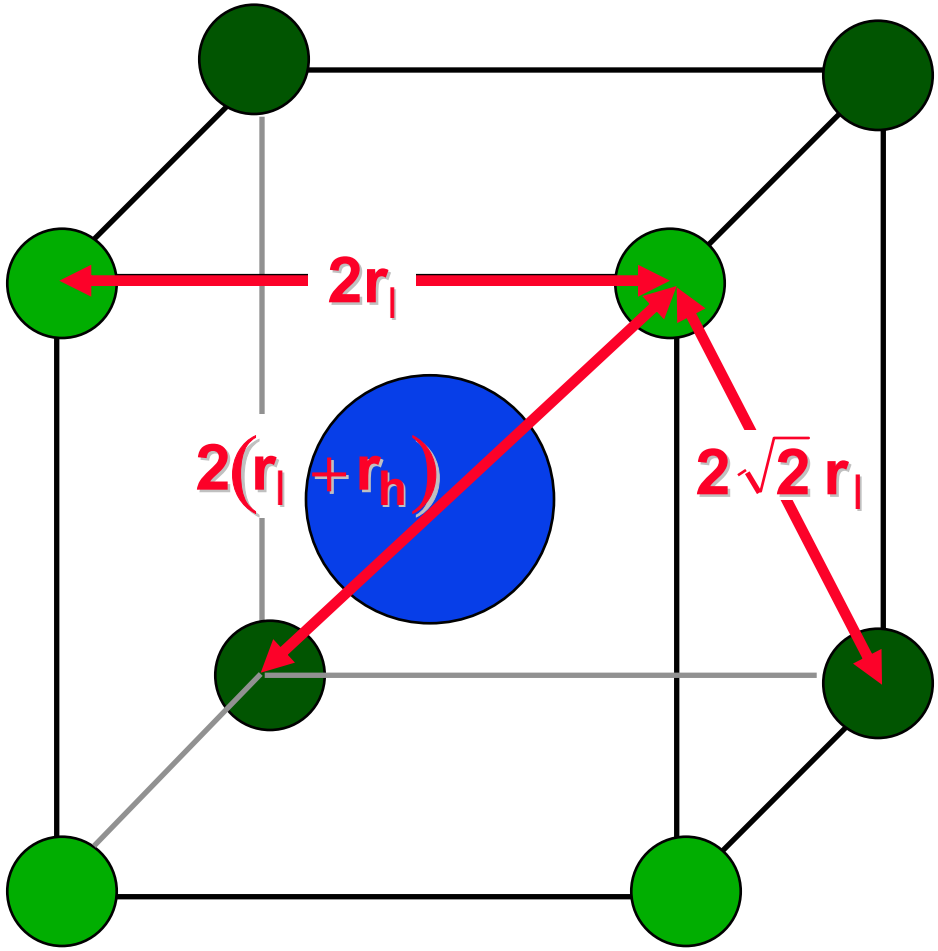
Geometry of Cubic Lattices

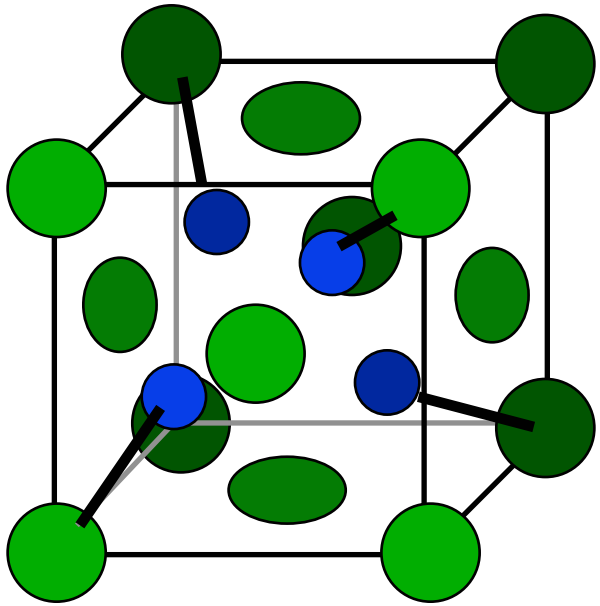


Geometry of Cubic Lattices



Geometry of Cubic Lattices

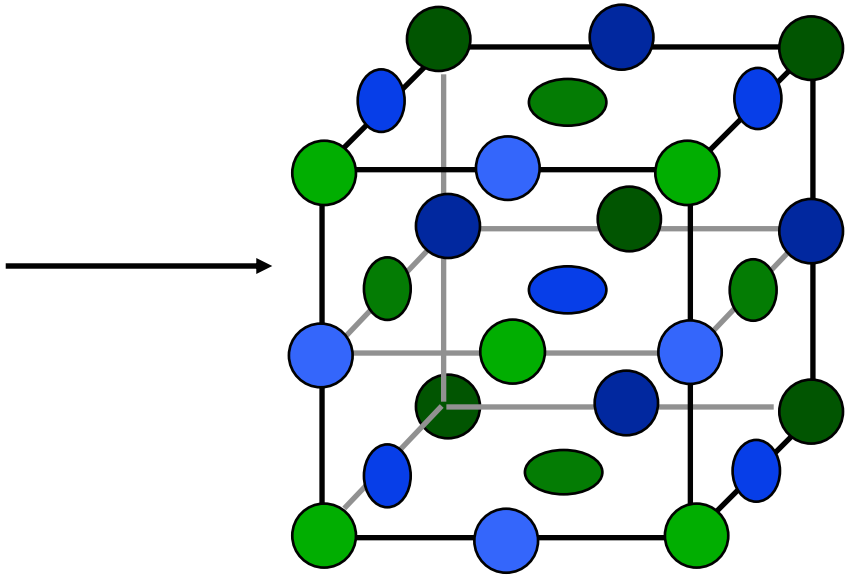




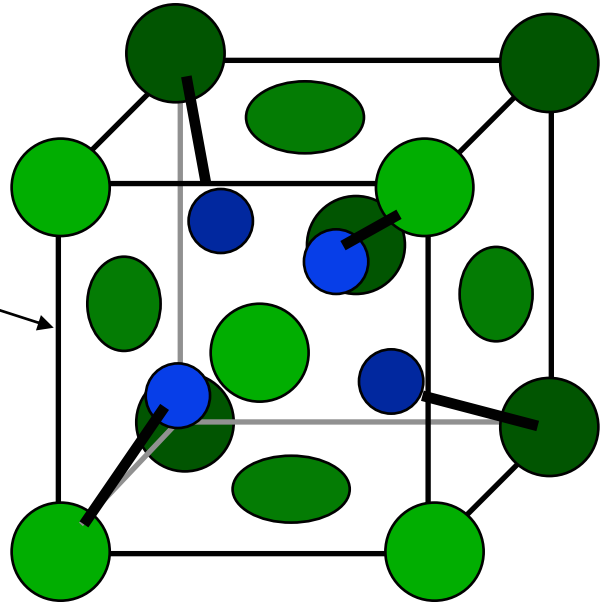
ZnS
(Smallest Cation/Anion)

NaCl
(Intermediate Cation/Anion)

Theory: 0.41
MgSe (0.33)
MgS (0.35)
CaTe (0.45)
MgO (0.46)
NaCl, all MX (M=Li, K, Na) except M=Cs
All CaS, MgS, MgSe, MY
KOH, KCN

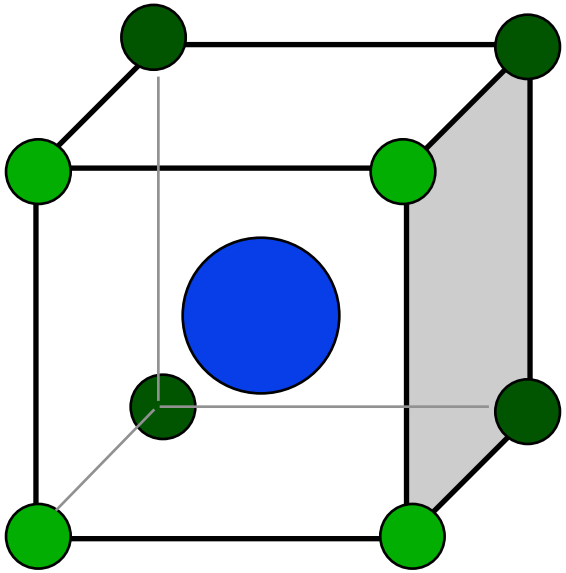


Theory: 0.23
BeO (0.22)
MgTe (0.29)
InP, GaAs
S, Se, Te salts
of Zn, Cd, Hg

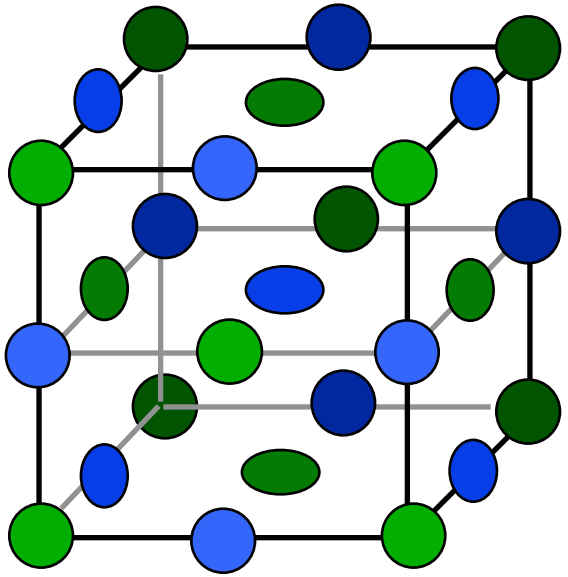


ZnS
(Smallest Cation/Anion)

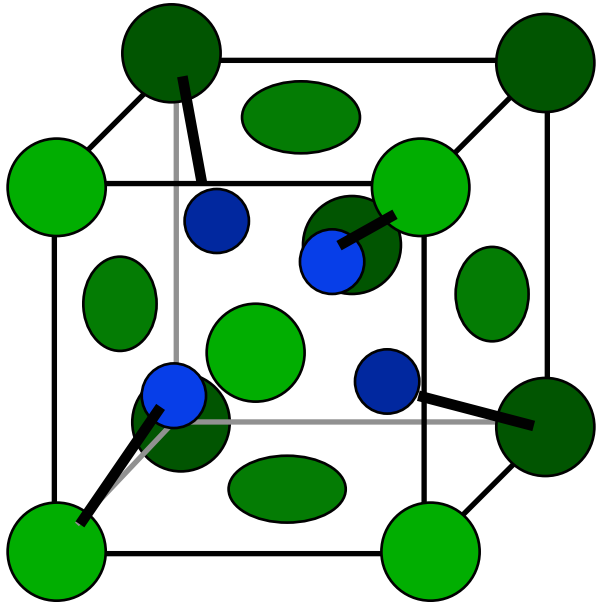
CsCl
(Biggest Cation/Anion)



NaCl
(Intermediate Cation/Anion)

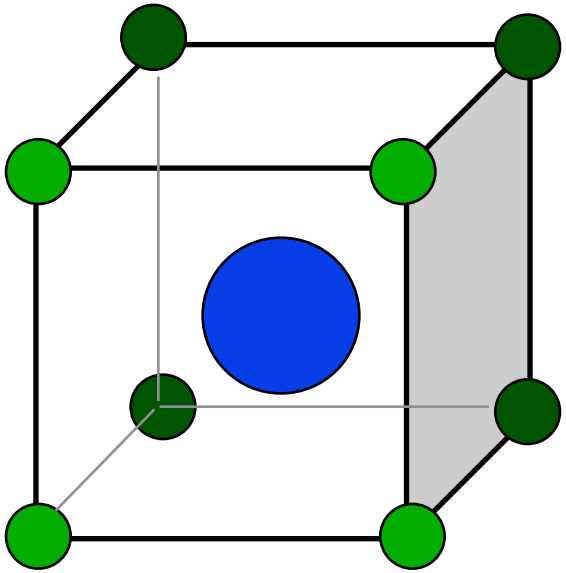


Theory: 0.75
Actual:
CsCl (0.93)
CsBr (0.87)

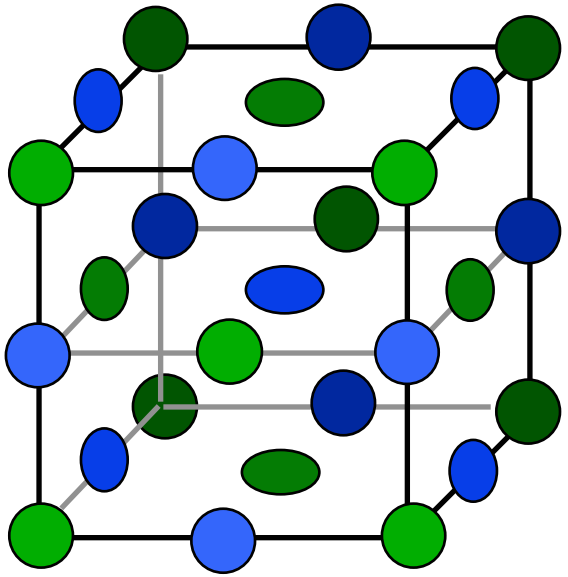


ZnS
(Smallest Cation/Anion)

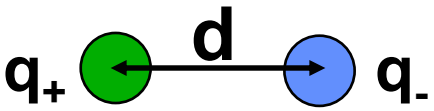
CsCl
(Biggest Cation/Anion)



NaCl
(Intermediate Cation/Anion)



Why Are Ionic Compounds So Stable?



Coulombic Attraction Between Point Charges:

$$E = \frac{(q_+)(q_-)e^2}{4\ \pi\ \varepsilon_o\ d}$$

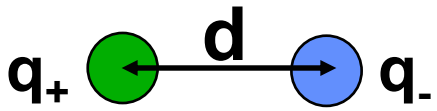
Repulsion Between Electron Clouds Goes Like

$$\frac{B}{d^n}$$

So Total Energy(E) vs. Distance(d) is:

$$E = \frac{(q_+)(q_-)e^2}{4\ \pi\ \varepsilon_o\ d} + \frac{B}{d^n}$$

What is the Equilibrium Distance (d_o)?



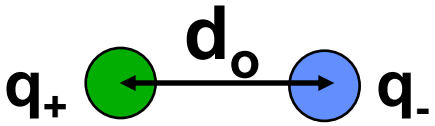
$$E = \frac{(q_+)(q_-)e^2}{4\ \pi\ \varepsilon_o\ d} + \frac{B}{d^n}$$

$$\frac{dE}{dd} = 0 \text{ when } E = E_{min}$$

Take the derivative; solve for B and plug in to find $E_{min} = E$ when $d = d_o$

$$E_{min} = \frac{(q_+)(q_-)e^2}{4\ \pi\ \varepsilon_o\ d_o}\left(1 - \frac{1}{n}\right)$$

What is the Equilibrium Energy (E_{min})?



$$E_{min} = \frac{(q_+)(q_-)e^2}{4\ \pi\ \varepsilon_o\ d_o}\left(1-\frac{1}{n}\right)$$

Plug in numbers:

$e = 1.6 \times 10^{-19}$

$q_+ = 1 \qquad q_- = -1$

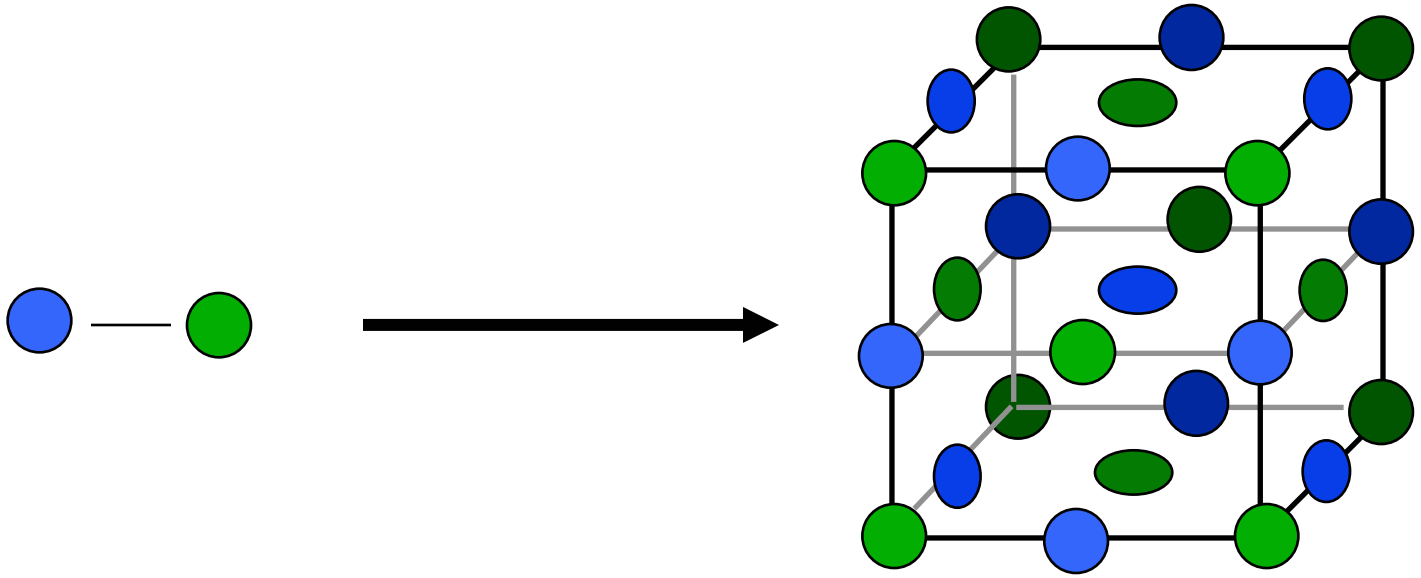
$d_o = 3 \times 10^{-10}$ m

$n = 9$

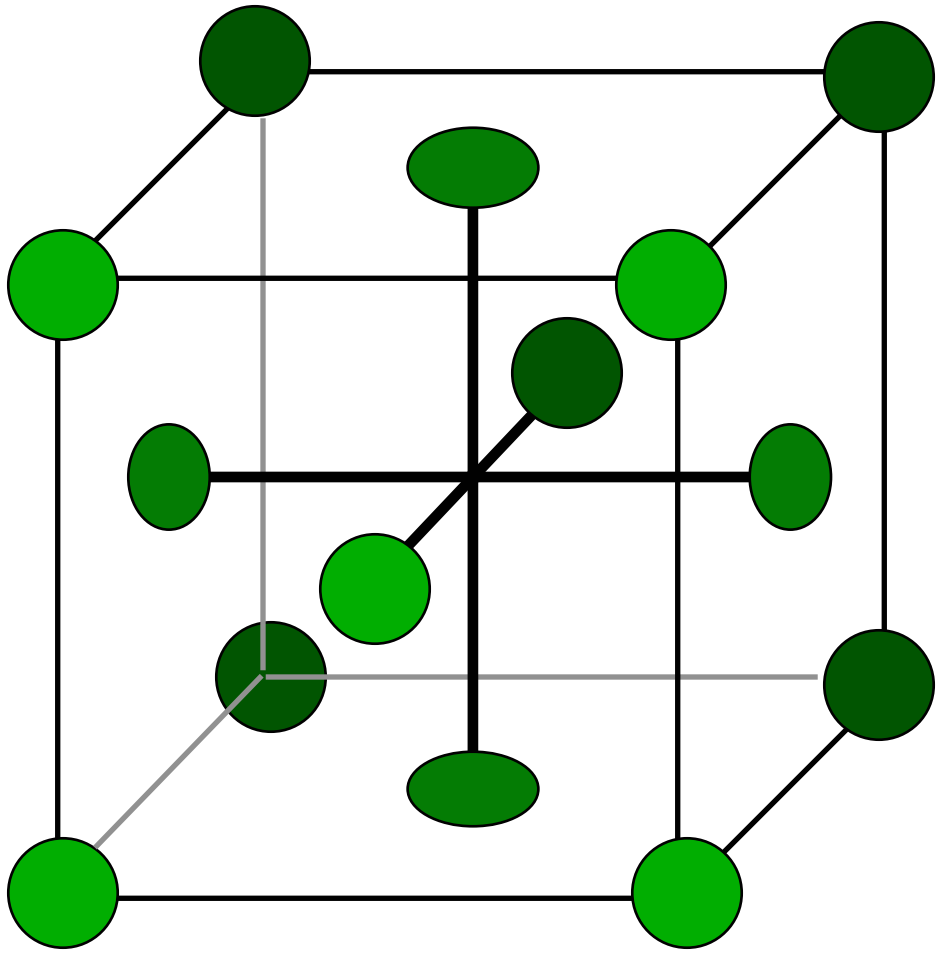
E_{min} = -400 kJ/mole

A VERY strong bond

Why is NaCl a solid and not a gas?

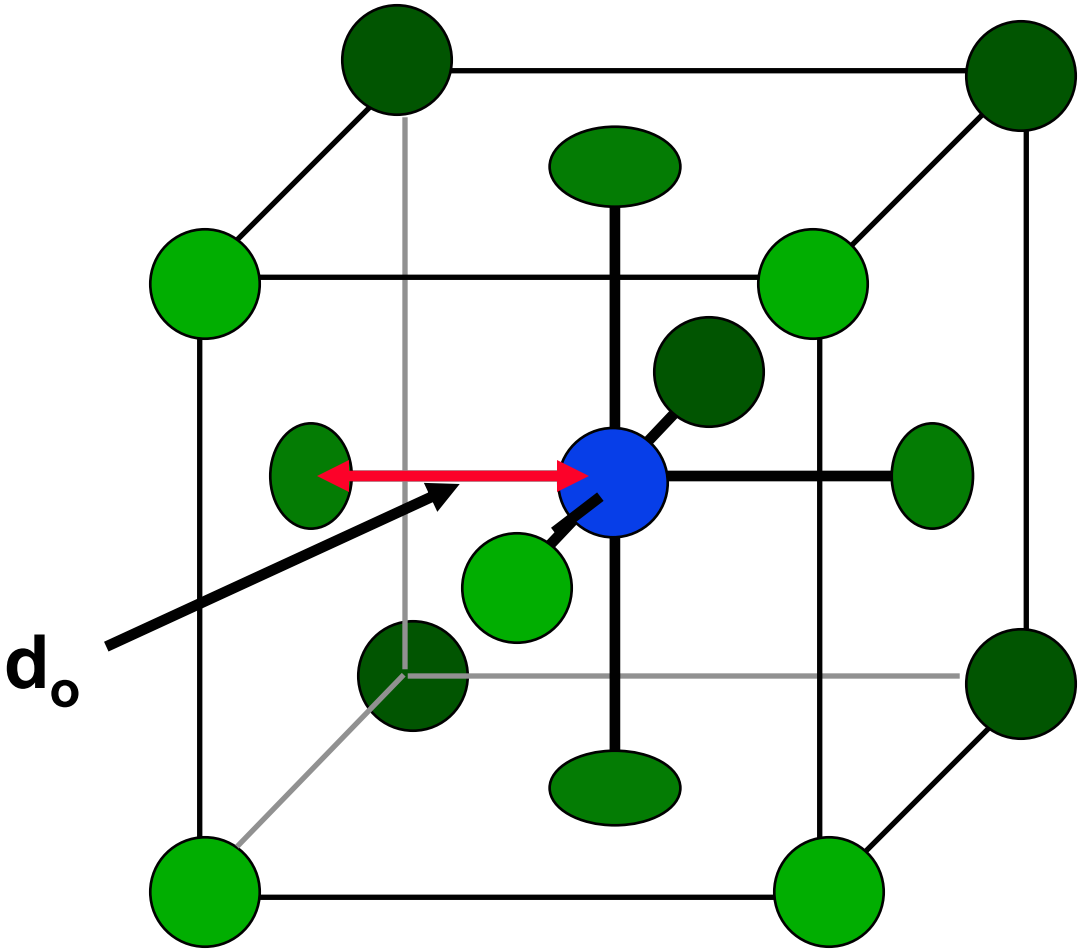


Consider the Coulomb Interactions



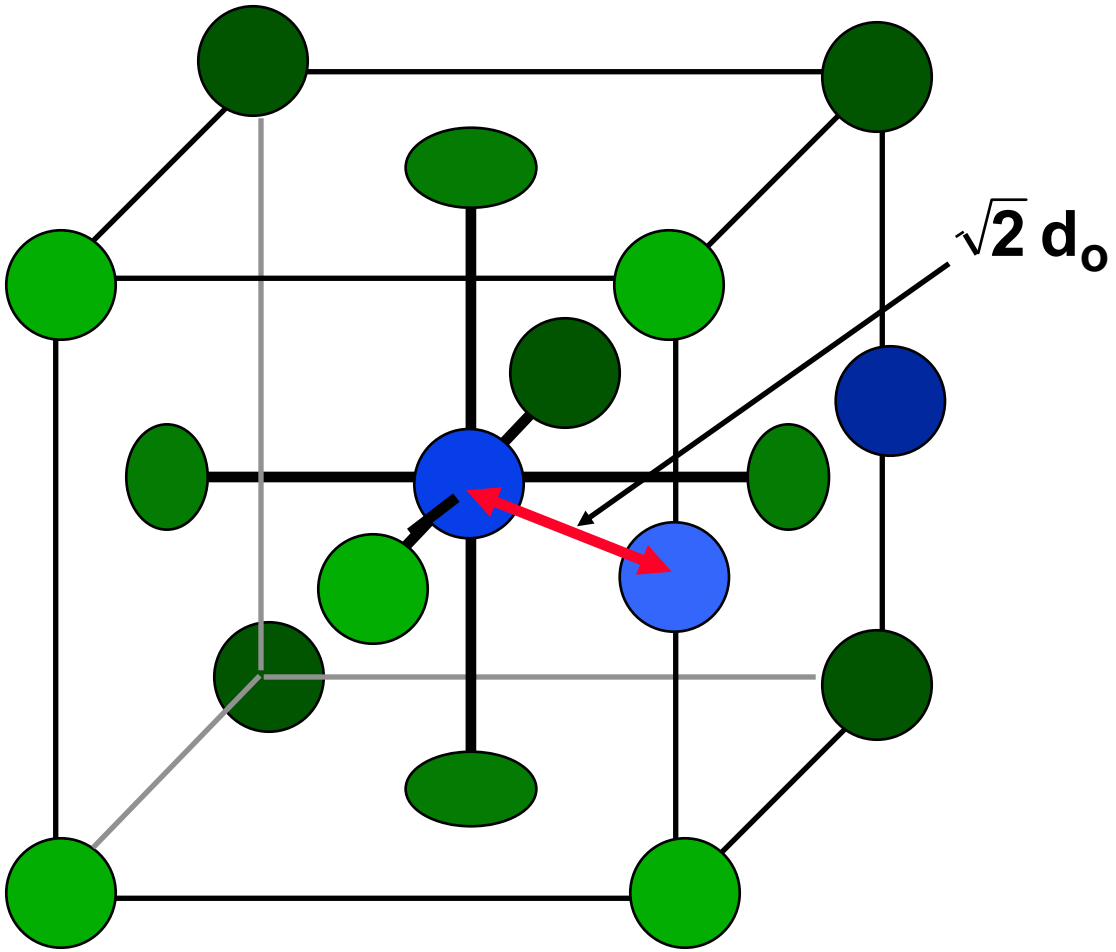
Hole is at Center of Unit Cell

Anion/Cation Attraction Energy: The Unique Octahedral Hole at Center



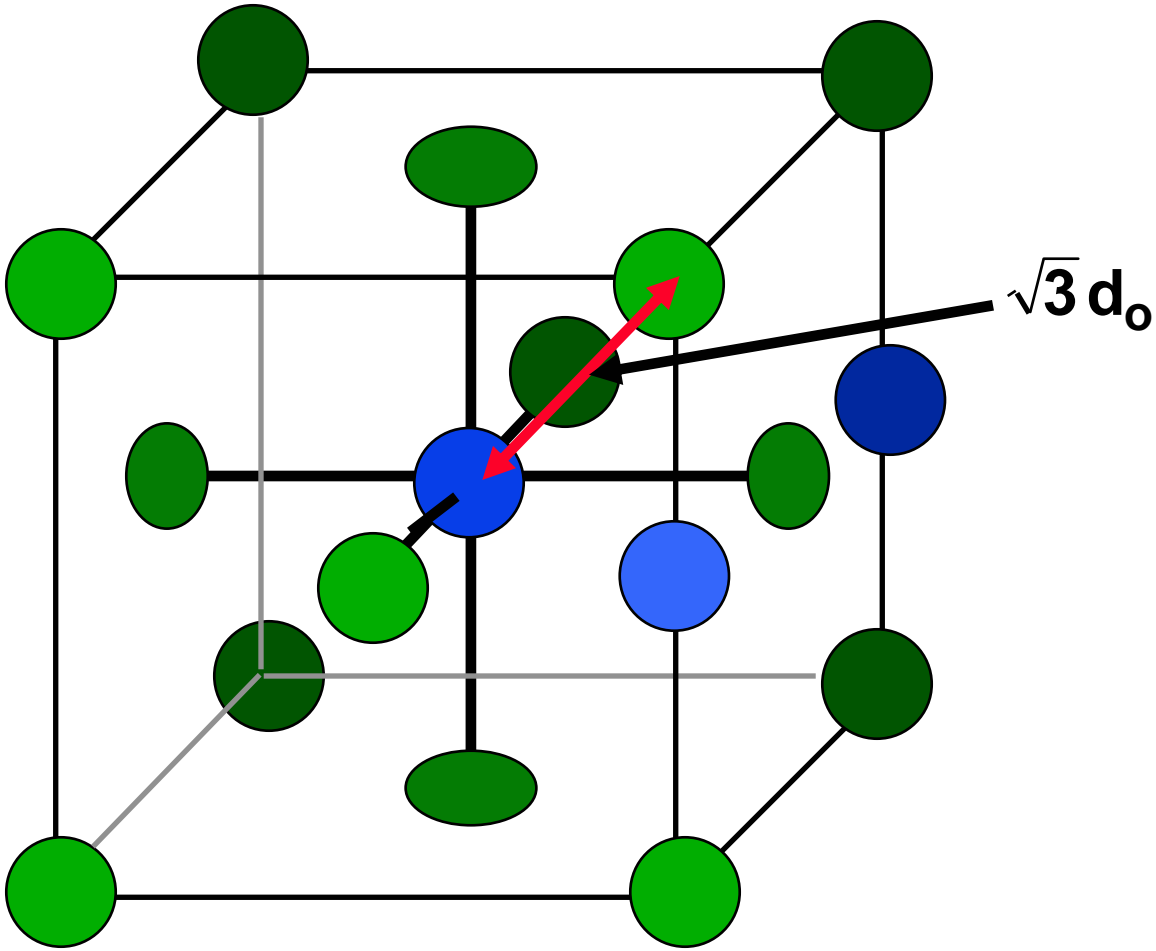
$$E_{min} = \frac{(q_+)(q_-)e^2}{4\ \pi\ \varepsilon_o\ d_o}\left(1-\frac{1}{n}\right) \times 6$$

Anion/Anion Repulsion Energy



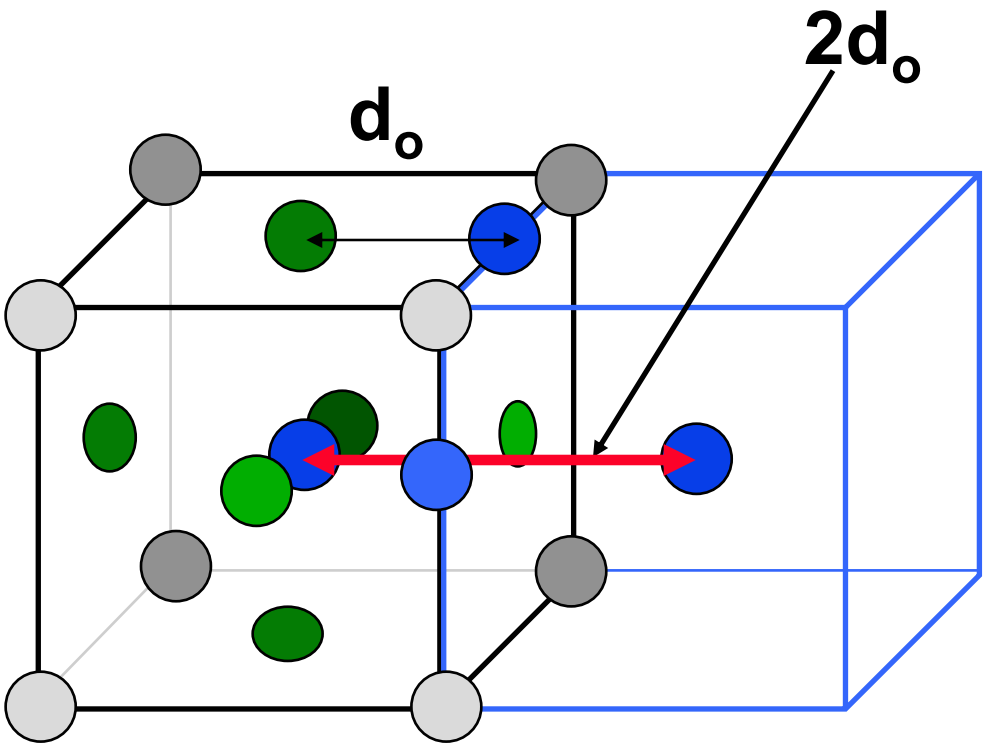
$$E_{min} = \frac{(q_+)(q_-)e^2}{4\ \pi\ \varepsilon_o\ d_o}\left(1-\frac{1}{n}\right)\left(6-\frac{12}{\sqrt{2}}\right)$$

More Anion/Cation Attraction Energy



$$E_{min} = \frac{(q_+)(q_-)e^2}{4\ \pi\ \varepsilon_o\ d_o}\left(1-\frac{1}{n}\right)\left(6-\frac{12}{\sqrt{2}}+\frac{8}{\sqrt{3}}\right)$$

More Anion/Anion Repulsion Energy



$$E_{min} = \frac{(q_+)(q_-)e^2}{4\ \pi\ \varepsilon_o\ d_o}\left(1-\frac{1}{n}\right)\left(6-\frac{12}{\sqrt{2}}+\frac{8}{\sqrt{3}}-\frac{6}{2}\right)$$

The Madelung Constant

$$E_{min} = \frac{(q_+)(q_-)e^2}{4\ \pi\ \varepsilon_o\ d_o}\left(1-\frac{1}{n}\right)\left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{2} + \ldots\right)$$

$$E_{min} = \frac{(q_+)(q_-)e^2}{4\ \pi\ \varepsilon_o\ d_o}\left(1-\frac{1}{n}\right) \times M$$

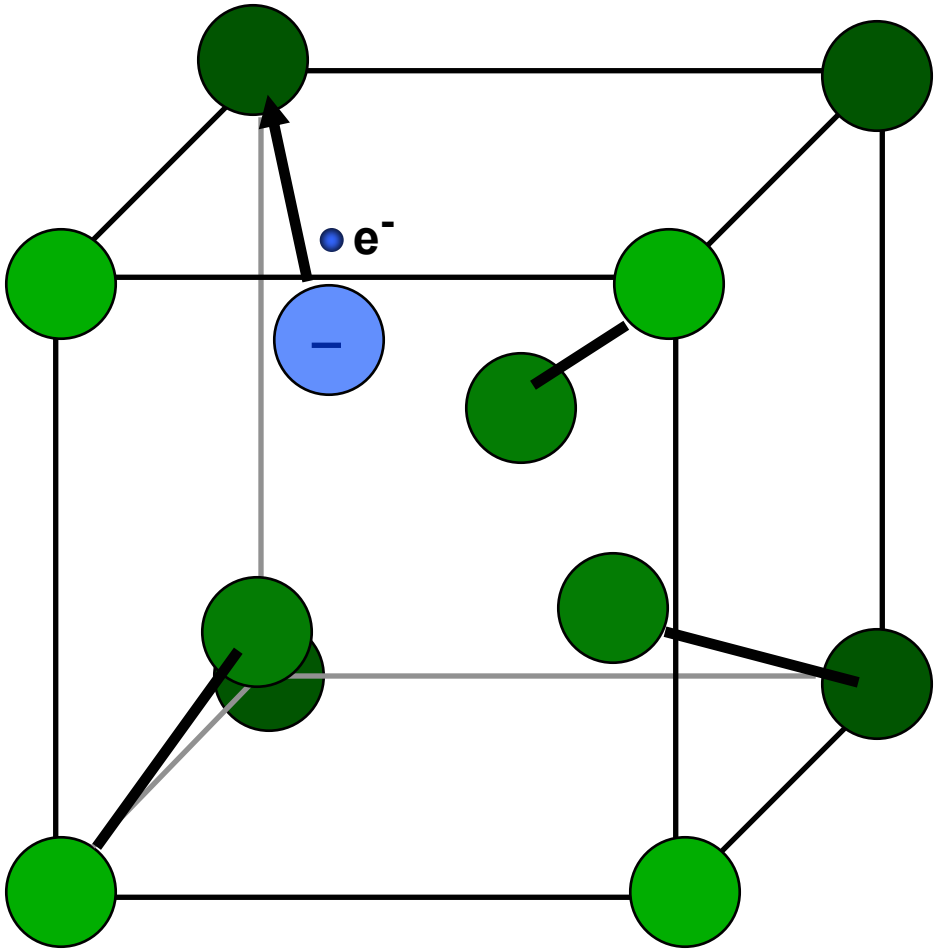
$$M = \left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{2} + \ldots\right) = 1.748$$

M is Extra Stability of Lattice Relative to the Energy of an Individual Molecule

Values of the Madelung Constant

Structure Type	M
NaCl	1.74756
CsCl	1.76267
Zinc Blende	1.63805
CaF_2 (Fluorite)	5.03878

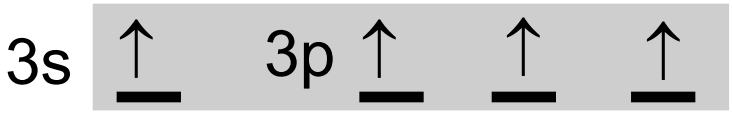
Doping Semiconductors



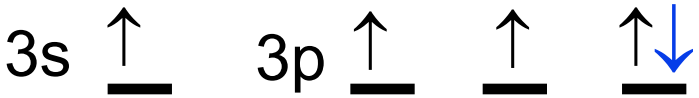
An Extra Free (Negative) Electron Forms an n-Type Semiconductor

Deducing Dopants From Periodic Trends

H																He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	**V**	**Cr**	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	**Nb**	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

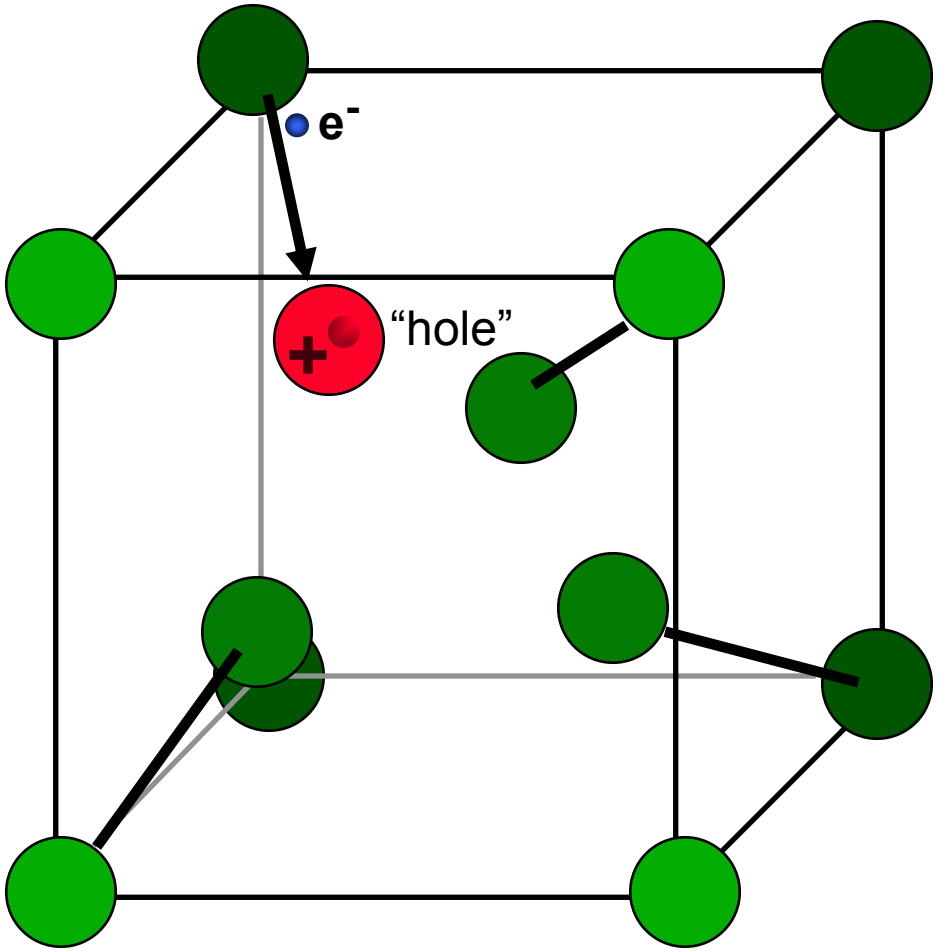


Si



P **(Donor)**

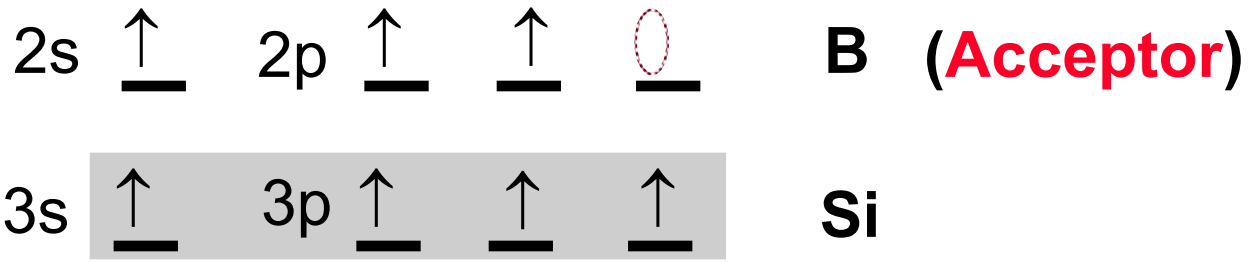
Doping Semiconductors



An Extra Electron Vacancy (Positive)
Forms a p-Type Semiconductor

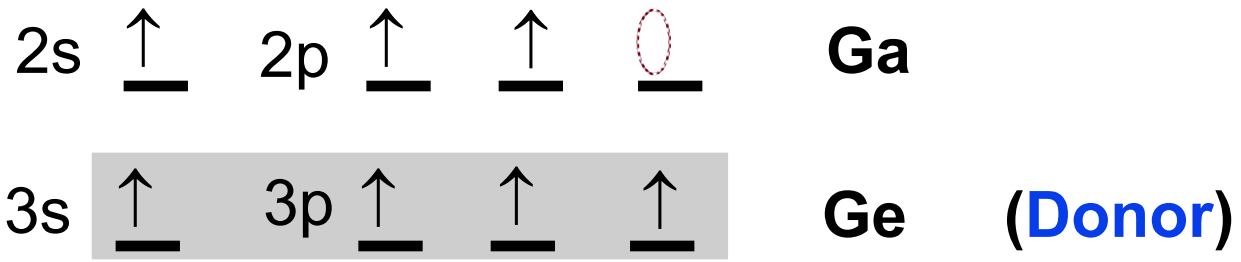
Deducing Dopants From Periodic Trends

H																He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	**V**	**Cr**	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	**Nb**	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															



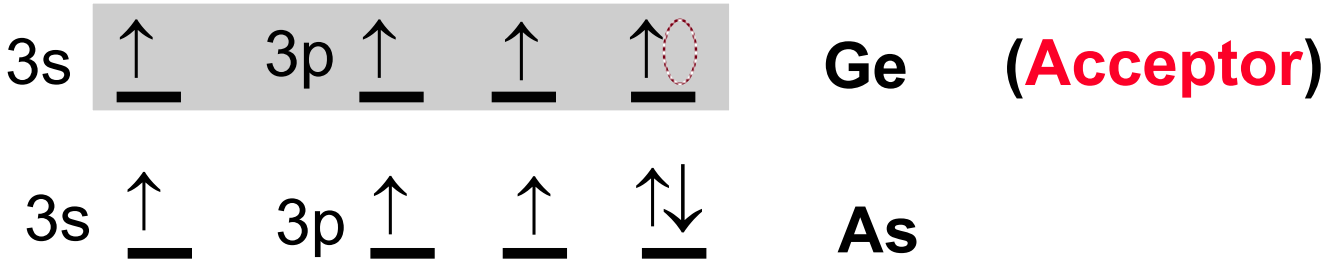
Deducing Dopants From Periodic Trends

H																He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	**V**	**Cr**	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	**Nb**	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															



Deducing Dopants From Periodic Trends

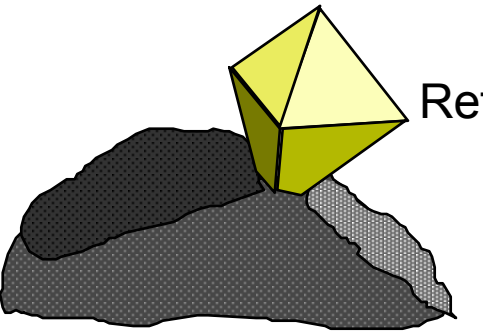
H																He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	**V**	**Cr**	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	**Nb**	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															



END

Crystals

Part 2



References: Gray: Chapter 6
OGN: Chapter 19 and (24.1)