Tohoku University Summer 2018

Advanced Tutorial in Materials Science & Engineering

Monday, Wednesday and Friday (1:00-2:30)
From June 11-July 13, 2018

Instructor: Fumio S. Ohuchi

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Advanced Tutorial in Materials Science and Engineering

Summer 2018: Intensive Lectures (5 weeks)
At Tohoku University, Sendai, Japan

1:00-2:30PM 3 times/week for 5 weeks (Monday, Wednesday and Friday)

この集中講義は現在ワシントン大学工学部物質材料学科で私が教鞭をとっている物質材料科学総論（大学院初年度学生向け）をもとにして作られたものです。 物質材料科学は今や理工各分野のすべてに浸透しユニークな発展をとげています。それだけに物質材料科学の全体像をもう一回レビューしてみよう、または専攻は違っても自分なりの物質材料科学を構築してみようと思われる学生諸君にこの集中講義は役に立つと思います。そこで この講義では物質材料科学の教科書の各論にそって講じるのではなく、原子配列や電子構造がどのようにそれぞれの物質の特性を決めお互いに関係しあっているか、熱力や運動論がどのように物質の構成を支配しているかなどの議論に焦点をあわせます。また固体材料に於ける格子点の原子・イオンの振る舞いに起因する特性の相関関係を色々な材料のデータから導き、任意の材料の特性を推論する手掛かりが得られるような関係式を導き出そうという新しい試みも導入します。今年は今までのCourse Packetを大幅に改定し、各チャプターの関連を強化し、これらの関連知識が学生諸君の将来の研究に役立つように最大限の工夫をしました。

講義は英語で行いますが、必要に応じて日本語も少し導入し言葉の壁を乗り越えて学生諸君と授業で交流します。この授業では、学生各個人が積極的に授業に参加してもらうことを期待してできるだけ授業はフレキシブルに行います。私は２５歳で渡米し今年でアメリカ在住４３年になりますが、 今までの私の色々な経験が学生諸君の何かに役に立てればと思いこの集中講義を開催します。奮って参加して下さい。

Course contents:

[0] Course introduction

PART-A

[I] Introduction: What's unique about Matls. Sci. and Eng?
[II] Atomistic arrangement and crystal structure
[III] Materials and bonding
[IV] Material's fundamental properties inferred from the lattice energy: A Volume-Based Thermodynamic (VBT) Approach
[V] Point defects and materials stability
[VI] Phase relation and transformation

PART-B

[VII] Materials under stress
[VIII] Electrical conduction and semiconductivity
[IX] Dielectric and optical properties
[X] Optical processes in semiconducting materials

Grading:

Midterm assignment & presentation	40%
Final exam (in-class exam)	40%
Class participation	20%

Pre-requisite:

No prerequisite is required to take this course, but the students are asked to prepare basic background by themselves.

Course pack:

Available for course attendees.
Additional supplements in pdf.

Suggested reference books for background information: Any of the following comprehensive text books introducing Materials Science and Engineering will serve as the reference for background.

- Charles A. Wert and Robb M. Thompson: *Physics of Solids*, McGraw-Hill Book Company.
- William D Callister, Jr. and David G. Rethwisch, *Materials Science and Engineering: An Introduction*, 6, 7 or 8th Editions, Wiley.
- James F. Shackelford, *Introduction to Materials Science for Engineers*, 6 or 7th Edition, Macmillan.
- L. H. Van Vlack, *Elements of Materials Science and Engineering*, 6th Edition,
- Craig R. Barret, William D. Nix and Alan S. Teleman, *The Principles of Engineering Materials*, Prentice-Hall, Inc. (classical book)

Sample Copies of Course Pack

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[IX] Dielectric and optical properties
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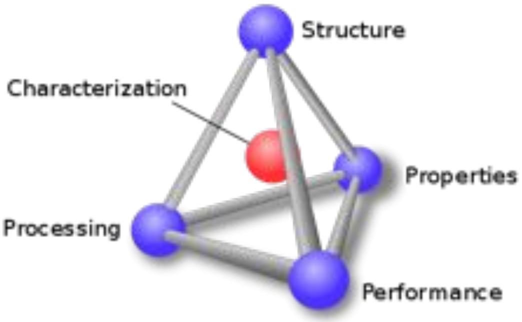
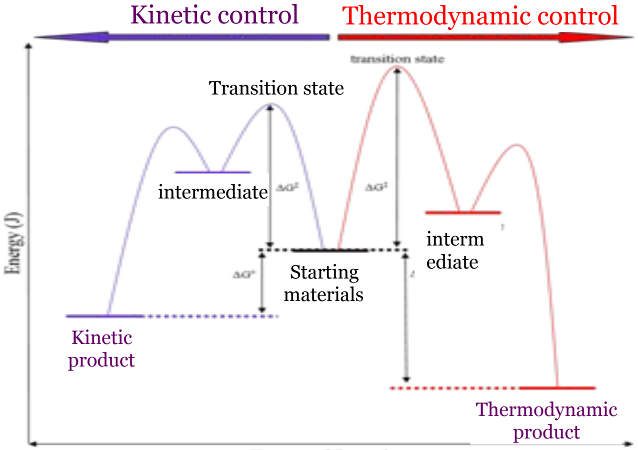
[I]
WHAT'S UNIQUE ABOUT MATERIALS SCI. & ENG.?



The concept of **materials science tetrahedron (MST)** concisely depicts the inter-dependent relationship among the structure, properties, performance, and processing of a material.

[I]. Thermodynamics and Kinetics

What do they tell us?

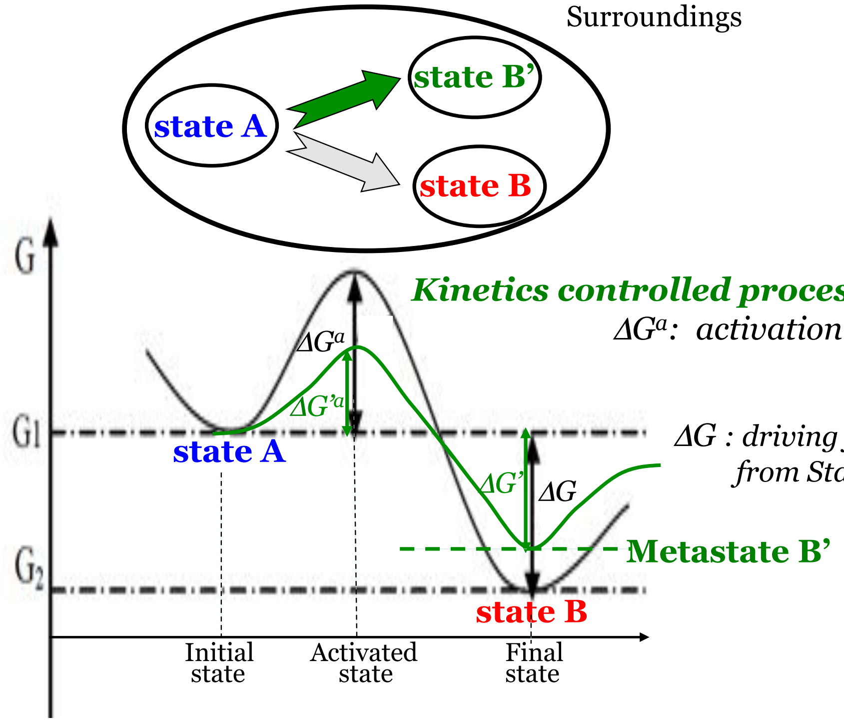


Kinetics
Describes reaction speed, whether it is at equilibrium and what factors effect the speed of the reaction

Tells you if it will get there in a reasonable amount of time.

Thermodynamics
Predicts distribution of chemical species and phases if reactions get to equilibrium (or final state)
Says nothing about speed of reaction, nor predict what can happen, but predict what cannot happen.

“Material Processing” is a thermodynamics, rate and kinetics convoluted process



Kinetics controlled process

ΔG^a: activation free energy barrier.

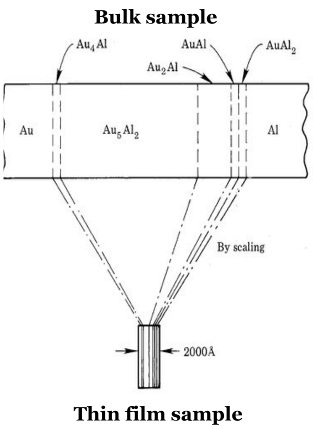
ΔG : driving force of transformation from State-A to State-B

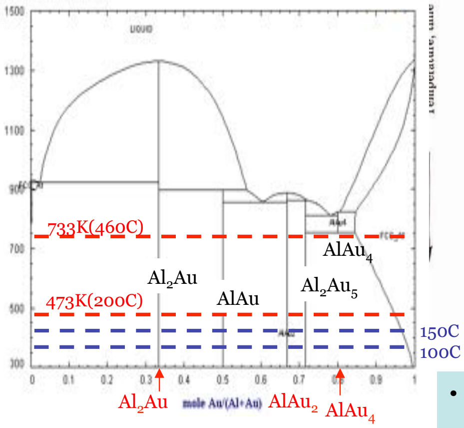
Thermodynamics vs. Kinetics

Example (1): Al-Au Bulk vs Thin Film

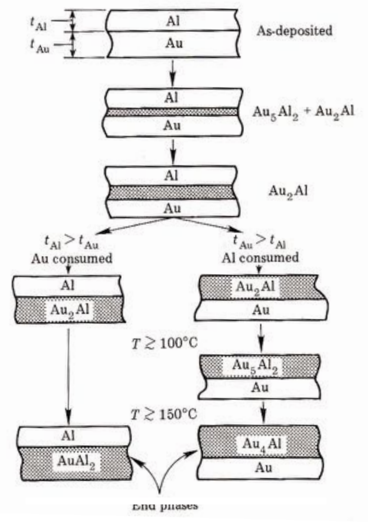
Bulk couple

- Annealed at 460C for 100min:
  All 5 compounds in correct order
- Annealed at 200C for 100min:
  $AuAl_2$ and AuAl are missing, other present





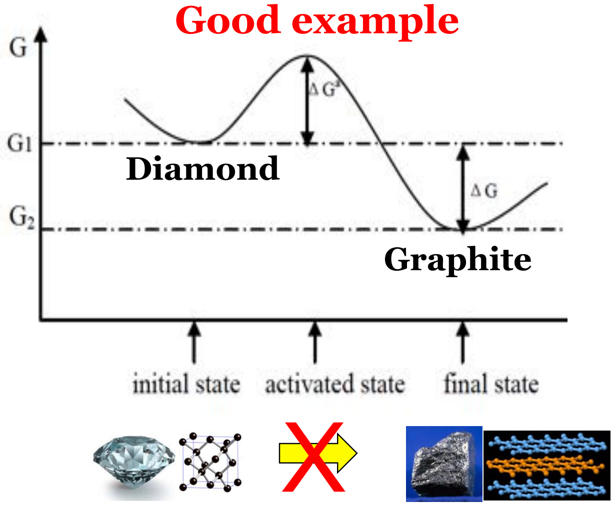
Thin film couple



- Reaction depends on thickness of each material
- Why are AlAu and Al_2Au_5 not seen?

Kinetics sometime controls the process

Good example



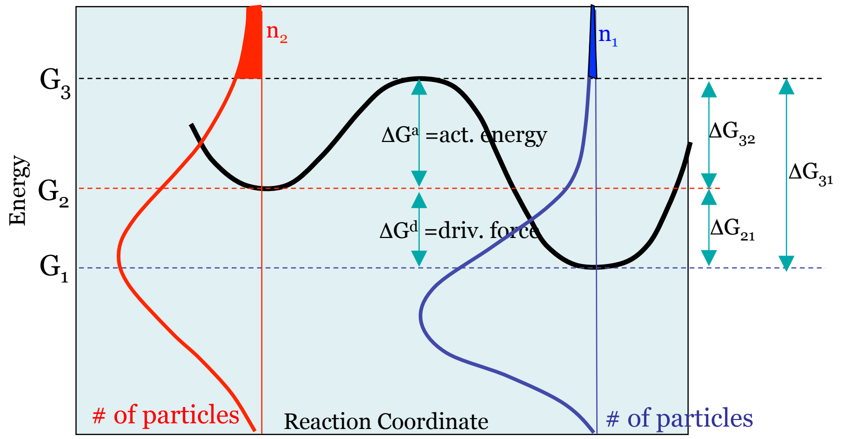
Thermodynamically favorable but kinetically unfavorable
This does not happen within your lifetime.

Rate: (Kinetic factor) x (Thermodynamic factor)

Activation energy (ΔG^a) Driving force ($\Delta G = G_2 - G_1$)

Take a chance: i.e., probability $= e^{-\Delta G^a/RT}$ If $\Delta G < 0$: highly happen!

A superimposed plot of Energy vs reaction coordinate, and Boltzmann Energy distribution in understanding the rate theory. Shaded areas give the number of atoms capable of surmounting over the activation barrier.



$$\text{The net reaction} = n_2 \exp(-\Delta G_{32}/kT) - n_1 \exp(-\Delta G_{31}/kT)$$
$$= \exp(-\Delta G_{32}/kT)\,[n_2 - n_1 \exp(-\Delta G_{21}/kT)]$$
$$= \exp(-\Delta G^a/kT)\,[n_2 - n_1 \exp(-\Delta G^d/kT)]$$

(1) If $\Delta G < 0$ then $\Delta G_{32} < \Delta G_{31}$ $\Rightarrow$ net reaction is in the forward direction.

(2) If the driving force is very large, $\Delta G << 0$ then $\Delta G_{32} << \Delta G_{31}$

$\exp(-\Delta G_{32}/kT) >> \exp(-\Delta G_{31}/kT) \Rightarrow$ net reaction rate $\approx n_2 \exp(-\Delta G_{32}/kT)$

(3) If the net reaction rate is zero, system reaches to dynamical equilibrium. Forward and backward reactions continue but equal number of particles are transferred in opposite directions $\Rightarrow$

$n_2 \exp(-\Delta G_{32}/kT) = n_1 \exp(-\Delta G_{31}/kT)$

$n_2/n_1 = \exp\{-\Delta G^d/kT\}$ = equilibrium constant

Rate Equation = ß F

ß: a system constant (diffusion constant, reaction rate, conductance etc.) The rate at which an atom or ion makes a jump.

F: is the driving force, a measure of how far a system is from equilibrium, or ΔG_d

Several important driving forces operative in Materials Science

- Reduction in free energies of formation as a result of chemical reactions and phase transformations,
  Example of consequence: **oxidation or crystallization**
- Reduction of energy due to applied stresses
  Example of consequence: **creep**
- Reduction of surface or interfacial energy,
  Example of consequence: **sintering and grain growth**
- Reduction of strain energy
  Example of consequence: **fracture, segregation**

Driving Forces Governing various Phenomena

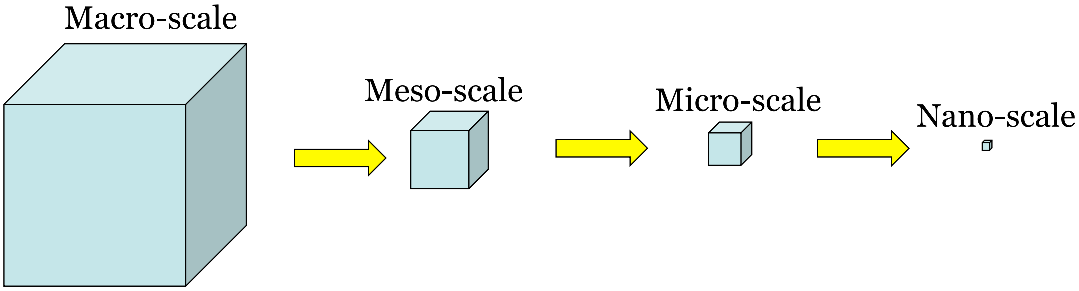
Rate of transformation: **Rate=βF**

Process	**Driving Force F**	**Typ. values (Joul/Mole)**	
Fracture	$V_m\sigma^2/(2Y)$	0.5	σ: stress at failure Y: Young's modulus
Grain growth	$2\gamma_{gb}/r$	20	γ_{gb}: grain boundary energy r: radius of a particle
Sintering	$2\gamma/r$	100	γ: surface energy r: curvature
Creep	σV_m	1000	σ: applied stress V_m: molar volume
Crystallization	$\Delta H \Delta T/T_m$	3000	ΔH : enthalpy of transf. ΔT : under cooling T_m : melting point
Inter diffusion	$RT(x_a \ln x_a + x_b \ln x_b)$	5000	Ideal solution
Oxidation	ΔG_{form}	50,000-500,000	Free energy of formation of oxide; a per-mole-of-O.

Assumptions : 1000K, molar volume: $10^{-5}m^3$/moll, r ~1μ, g=1J/m^2. σ=100MPa

[III]. Length Scale in MSE

Why smaller scale?

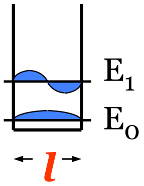


- Quantum physics kicks in when structures become smaller than the wavelength of an electron in a solid.
- The electrons get squeezed into a “quantum box” and have to adapt to the shape of the solid by changing their wave function.
- Their wavelength gets shorter, and that increases their energy.
- Since the wave function of the outer electrons determines the chemical behavior, one is able to come close to realizing the medieval alchemist’s dream of turning one chemical element into another.

Fundamental Length Scales

Quantum

Quantum Well:
Quantum Well Laser

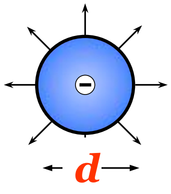


Energy Level Spacing:

$E_1 - E_0 = 3h^2/8m\,l^2 > k_BT$

Electric

Capacitor:
Single Electron Transistor



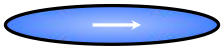
Charging Energy

$E_C = 2e^2/\varepsilon\, d > k_BT$

$\varepsilon = 12$ for silicon

Magnetic

Magnetic Particle:
Data Storage Media



Magnetic energy barrier

$a = V^{1/3}$

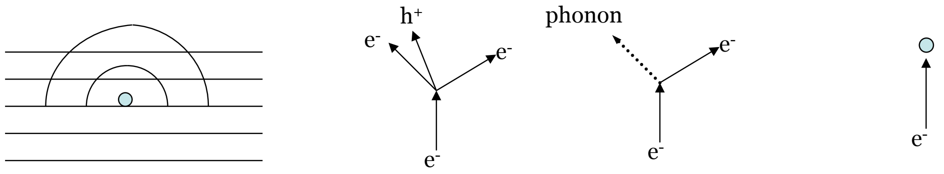
Spin Flip Barrier

$E_M = \frac{1}{2} M^2 a^3 > k_BT$

$l < 7$ nm $\quad$ $d < 9$ nm $\quad$ $a > 3$ nm

Scattering Length Scale

Elastic	Inelastic		
$\Delta E = 0$	$\Delta E > 0$		
Scattering Potential → Diffraction, Phase Shift	Electron-Electron	Electron-Phonon	Trapping at an Impurity



	Electron-Electron	Electron-Phonon	Trapping at an Impurity
Semiconductors:	long	long	≈ 10 nm
Metals:	long	≈ 1000 nm	≈ 100 nm (Room temperature, longer at low temp.)

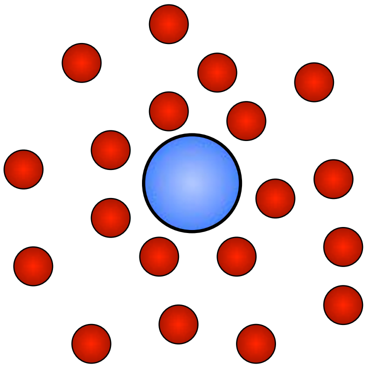
Consequences:

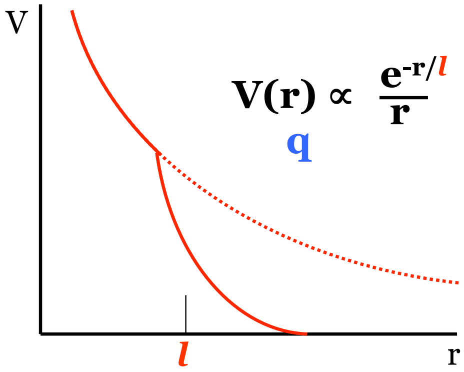
- Ballistic electrons at small distances (extra speed gain in small transistors)
- Recombination of electron-hole pairs at defects (energy loss in a solar cell)
- Loss of spin information (optimum thickness of a magnetic hard disk sensor)

Screening Lengths

$l \sim 1/\sqrt{n}$ (**n** = Density of screening charges)

Metals:	Semiconductors:	Electrolytes:
Electrons at E_{Fermi}	Electrons, Holes	Ions
Thomas-Fermi s. l.	Debye s. l.	Dbye-Hückel s.l.
0.1 nm	1-1000 nm	0.1-100 nm





$$V(r) \propto \frac{e^{-r/l}}{r}$$

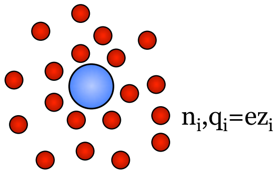
Exponential cutoff of the Coulomb potential (dotted) at the screening length l.

Length Scales in Electrochemistry

Screening

Debye-Hückel Length

Electrolyte



$$l_{DH} = (\varepsilon\, k_B T / 4\pi\, \Sigma n_i q_i^2)^{1/2}$$
$$= 1 / (4\pi\, l_B\, \Sigma n_i z_i^2)^{1/2}$$

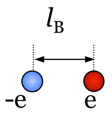
0.1 Molar Na^+Cl^-

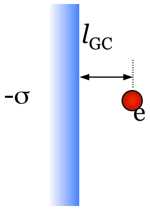
l_{DH} = **1.0** nm

Electric: $E_{Coulomb} = k_B T$

Bjerrum Length, Gouy-Chapman Length

Dielectric





$$l_B = e^2 / \varepsilon\, k_B T \;, \qquad l_{GC} = 2 / l_B\, e\, \sigma$$
$$= r_{Coulomb}$$

Pure H_2O

l_B = **0.7** nm

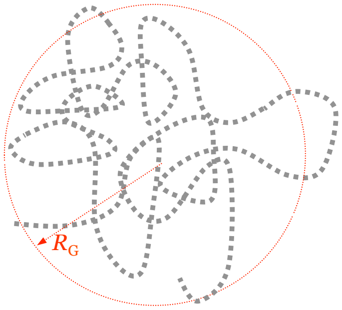
Length Scales in Polymers

(including Biopolymers, such as DNA and Proteins)

Random Walk, Entropy

Radius of Gyration

(overall size, N straight segments)



$$R_G \propto l_P \sqrt{N}$$

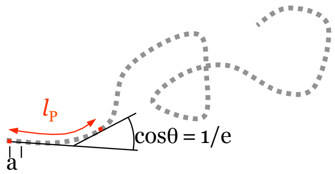
Copolymers

$R_G \approx$ **20-50** nm

Stiffness α vs. $k_B T$

Persistence Length

(straight segment)



$$l_P = \alpha / k_B T$$

DNA (double)

$l_P \approx$ **50** nm

Polystyrene

$l_P \approx$ **1** nm

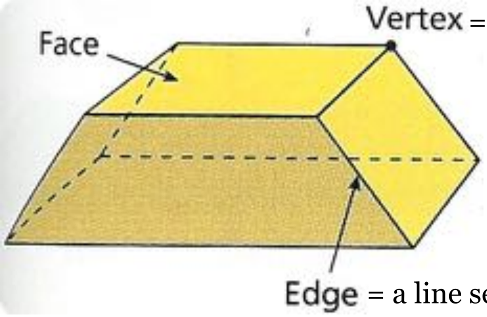
[II]
ATOMISTIC ARRANGEMENT & CRYSTAL STRUCTURES

- How do atoms assemble into solid structures?
- How does the density of a material depend on its structure?
- When do material properties vary with the sample (i.e., part) orientation?
- The properties of some materials are directly related to their crystal structures.
- Significant property differences exist between crystalline and noncrystalline materials having the same composition.

Back ground	MSE 170 (Callister: Chapters 3, 12, 14)
UG course	MSE 331 (Crystallography and XRD)
Grad courses	MSE 510 MSE 518

[I]. POLYHEDRONS

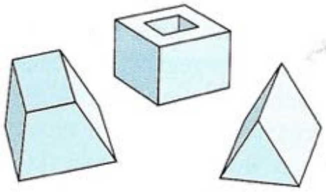
A **POLYHEDRON** is a solid that is bounded by polygons (**faces**) that enclose a single region of space.



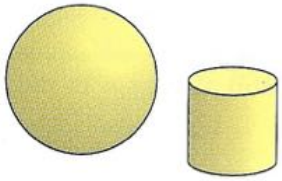
Vertex = a point where three or more edges meet

Edge = a line segment formed by the intersection of two faces

Which of these are Polyhedrons?

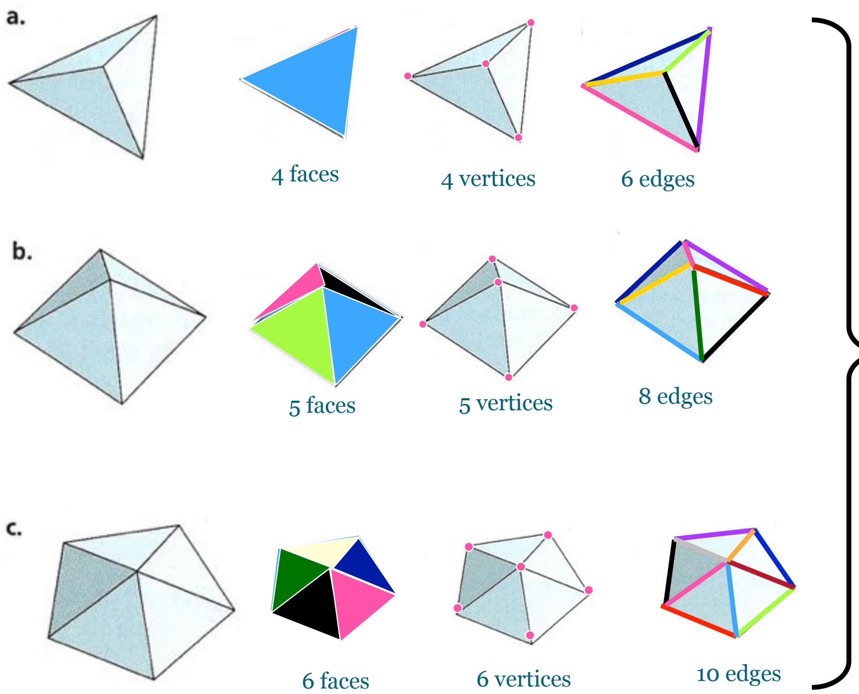


These are polyhedrons.



These are not polyhedrons.

Count the faces, vertices, and edges of each polyhedron



4 faces
4 vertices
6 edges

5 faces
5 vertices
8 edges

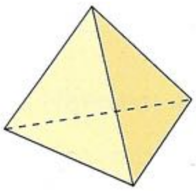
6 faces
6 vertices
10 edges

$F + V = E + 2$

Euler's Theorem

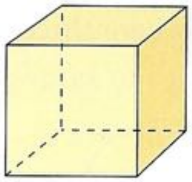
The Platonic Solids

Five kinds of Regular, Convex Polyhedrons
First described by Plato (350BC)



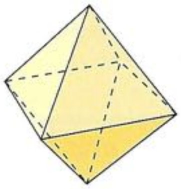
Regular tetrahedron

4 faces



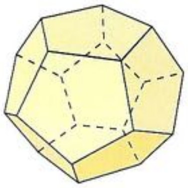
Cube

6 faces



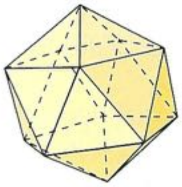
Regular octahedron

8 faces



Regular dodecahedron

12 faces



Regular icosahedron

20 faces

[III]. CRYSTALLOGRAPHY BASICS

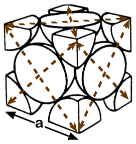
Summary Only

Assume everyone know the basis of crystallography

Counting Atoms & Lattice Points

$$N_A = N_I + N_F/2 + N_E/4 + N_C/8$$

N_I = # with centers at interior points.
N_F = # with centers at face centers.
N_E = # with centers on cell edges.
N_C = # with centers on cell corners.



Point Indices

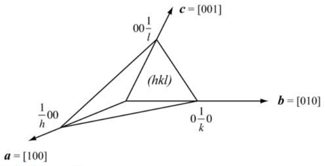
$\mathbf{T} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$ primitive cell vectors **a**, **b**, **c**, not a Cartesian coordinate system

Example: In any crystal system, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ = body center $\frac{1}{2}\frac{1}{2}0$ = a face center $\frac{1}{2}\frac{1}{2}1$ = a face center

Direction Indices

[uvw]

specific vector from the origin to point uvw
any vector || to it and of equal length and magnitude.

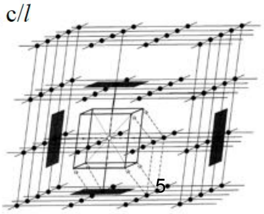


Planes

(hkl)

specific plane, whose intercepts with **a**, **b**, **c** are at a/h, b/k, c/*l*

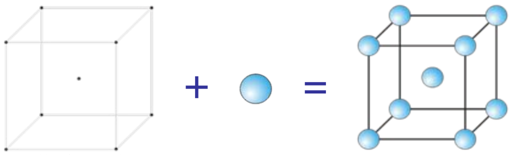
	Specific	Family
Planes	(hkl)	{hkl}
Directions	[uvw]	<uvw>



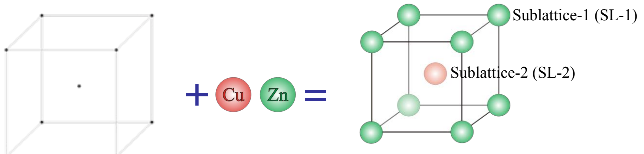
How do you describe "CRYSTAL"?

Crystal = Lattice + Motif

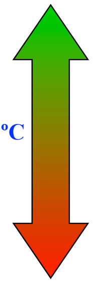
(Where to repeat?) (What to repeat?)

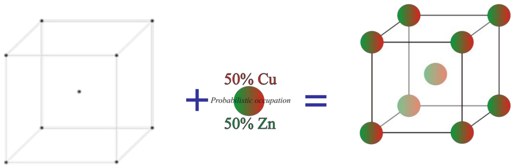


Unit cell of BCC lattice



Unit cell of BCC lattice





Unit cell of BCC lattice

Crystal = Space group + Asymmetric unit

(How to repeat?) (Motif': what to repeat?)

Real Lattice vs. Reciprocal Lattice

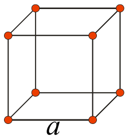
Student's FACT: The concepts of reciprocal lattice, structure factor calculations often 'strike terror' in the hearts of students!

- ❑ From the real lattice the reciprocal lattice can be *geometrically constructed*☺. The properties of the reciprocal lattice are 'inverse' of the real lattice
  → planes 'far away' in the real crystal are closer to the origin in the reciprocal lattice.
- ❑ A real crystal can be thought of as decoration of a lattice with motif.
  A reciprocal crystal can be visualized as a Reciprocal Lattice decorated with a motif* of Intensities (structure factor)

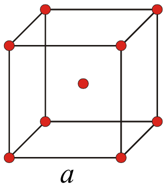
  Real Crystal = Real Lattice + Motif
  Reciprocal Crystal = Reciprocal Lattice + Intensities as Motif*
- ❑ The reciprocal of the 'reciprocal lattice' is nothing but the real lattice!
- ❑ ***Planes*** in real lattice become ***points*** in reciprocal lattice and vice-versa.

Real Space

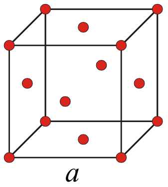
SC crystal



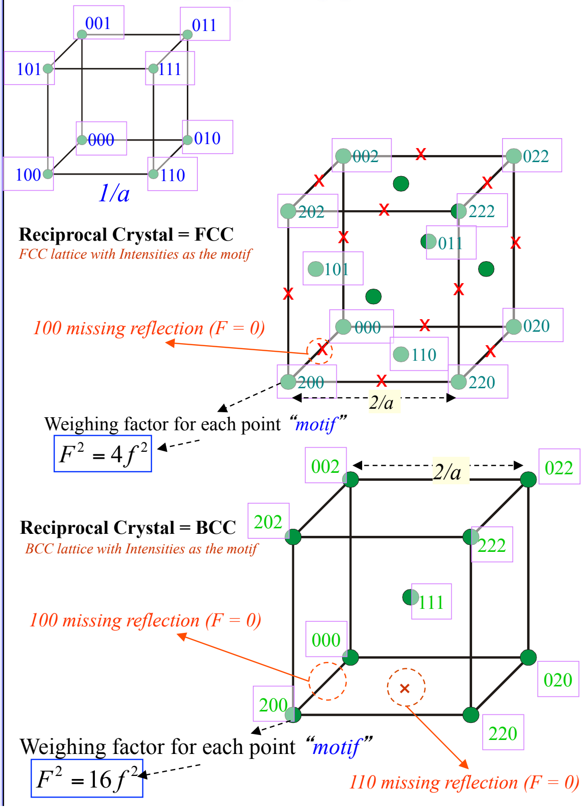
BCC crystal



FCC crystal



Reciprocal Space



Reciprocal Crystal = FCC

FCC lattice with Intensities as the motif

100 missing reflection (F = 0)

Weighing factor for each point *"motif"*

$\boxed{F^2 = 4f^2}$

Reciprocal Crystal = BCC

BCC lattice with Intensities as the motif

100 missing reflection (F = 0)

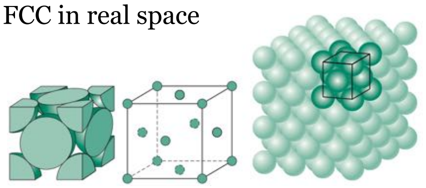
Weighing factor for each point *"motif"*

$\boxed{F^2 = 16f^2}$

110 missing reflection (F = 0)

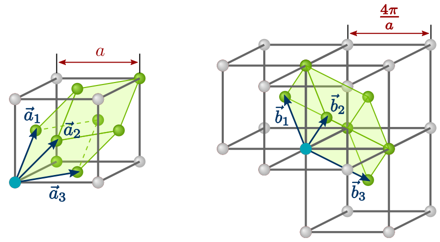
Real vs. Reciprocal Space

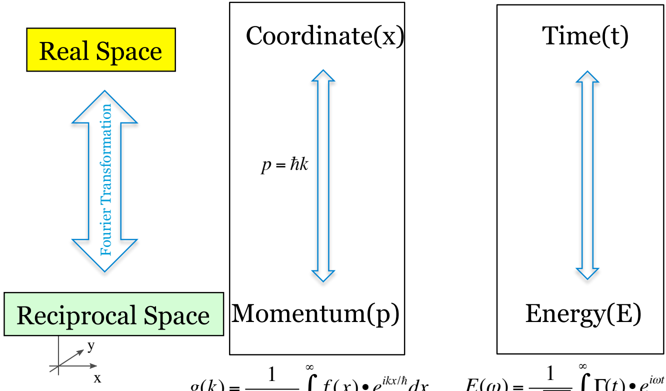
FCC in real space



direct lattice:
fcc with edge length a

reciprocal lattice:
bcc with edge length 4π/a





Conjugate Variables

Real Space

Fourier Transformation

Reciprocal Space

Coordinate(x)

$p = \hbar k$

Momentum(p)

Time(t)

Energy(E)

$$g(k) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} f(x) \bullet e^{ikx/\hbar} dx$$

or

$$f(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} g(k) \bullet e^{ikx/\hbar} dk$$

$$E(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Gamma(t) \bullet e^{i\omega t} dt$$

or

$$\Gamma(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} E(\omega) \bullet e^{i\omega t} d\omega$$

- Conjugate variables to connect real and reciprocal spaces are (x, p) and (E, t).
- There must be a momentum space equivalent to the unit cell.
- This is called by "**Brillouin zone (BZ)**".
- First BZ is just like an unit cell of the momentum space, so whole energy space can be projected into the first BZ.

[III]. METALLIC CRYSTAL STRUCTURES

(1) Tend to be densely packed.

(2) Reasons for dense packing:

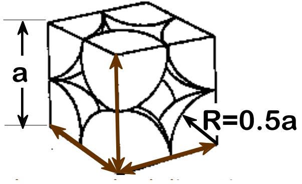
- Typically, only one element is present, so all atomic radii are the same.
  Metallic bonding is not directional.
  Nearest neighbor distances tend to be small in order to lower bond energy.
- The "electron cloud" shields cores from each other

(3) Metals have the simplest crystal structures.

SC

CN# = 6

ex: Po(only known)

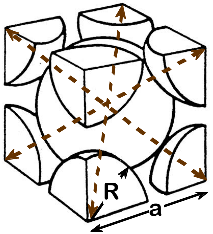


8 x 1/8
=1 atoms/unit cell

BCC

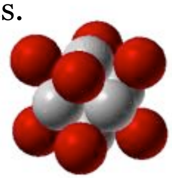
CN# = 8

ex: Cr, W, Fe (α), Ta, M



8 x 1/8 + 1
=2 atoms/unit cell

FCC

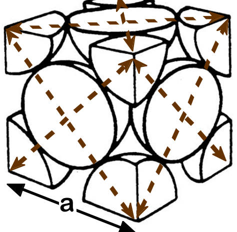


↔ HCP

CN# = 12

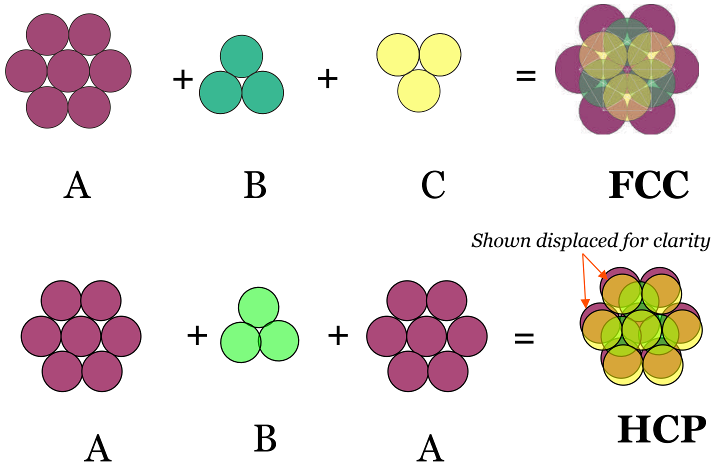
ex: Al, Cu, Au, Pb, Ni, Pt, Ag

ex: Mg, Ti, Zr, Hf, Zn

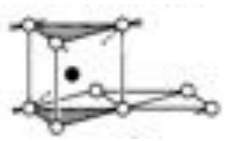


8 x 1/8 + 6x 1/2
=4 atoms/unit cell

Energy difference between FCC and HCP stacking



Trigonal-prismatic
NbS_2, $TaSe_2$, MoS_2, WSe_2



Octahedral
TiS_2, ZrS_2, $TiSe_2$, TaS_2

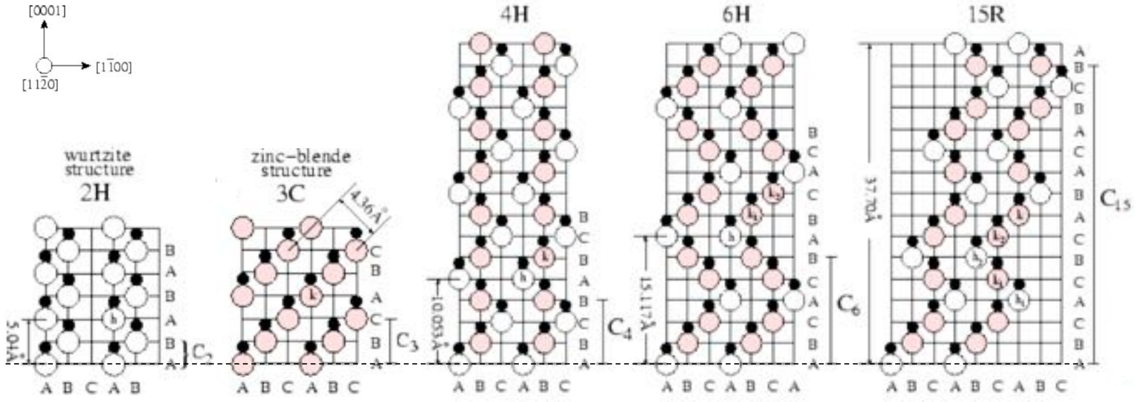
- Crystals made up of stacking of 2-D hexagonal close-packed layers differ in **entropy** by only ~$10^{-3}k_B$ per sphere.
- 1^{st} nearest neighbors: No difference;
  2^{nd} nearest neighbors: Tiny but real difference

T=300˚K ~$10^{-3}k_BT=2.6\times10^{-7}$eV/sphere

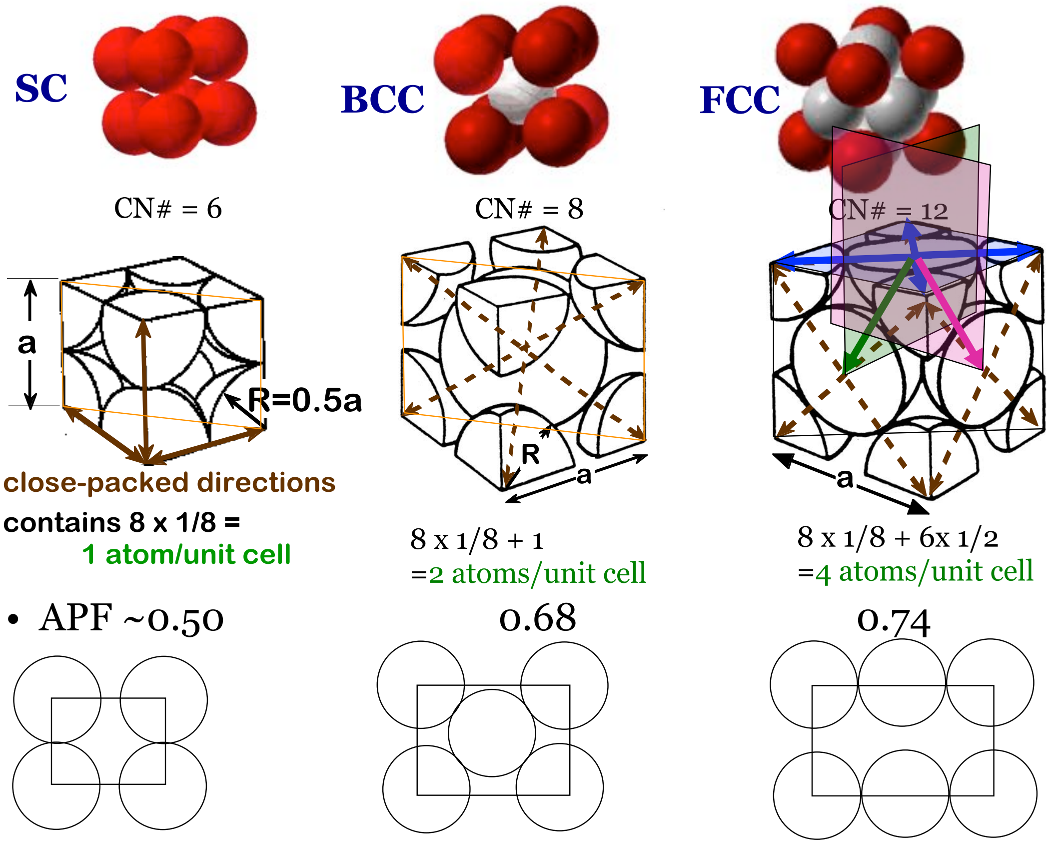
- An ultimate test of accuracy in atomistic computations
- For 10,000atoms, ΔE~2.6meV.

- Packing density is the same for FCC and HCP (74%)
- Use these differences for testing ultimate accuracy in computations.

FCC and HCP stacking: Where can you see? Polytypes in SiC



	3C-SiC	4H-SiC	6H-SiC	15R-SiC
Band Gap (eV)	2.390	3.265	3.023	2.986
Lattice const (Å)	4.36	3.08/10.05	3.08/15.12	3.08/37.70
m_e (electron)*/m_0	0.68	0.37	0.69	0.53/0.25
m_h (hole)*/m_0		0.94	0.92	
μ_e(cm^2/V•sec)	900	500	300	400
μ_h(cm^2/V•sec)	20	50	50	



SC

BCC

FCC

CN# = 6

CN# = 8

CN# = 12

close-packed directions

contains 8 x 1/8 =
1 atom/unit cell

8 x 1/8 + 1
=2 atoms/unit cell

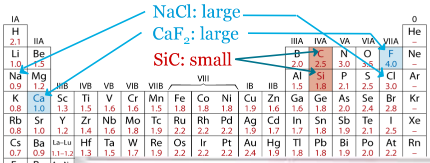
8 x 1/8 + 6x 1/2
=4 atoms/unit cell

- APF ~0.50

0.68

0.74

[VI]. TYPE OF CERAMIC MATERIALS

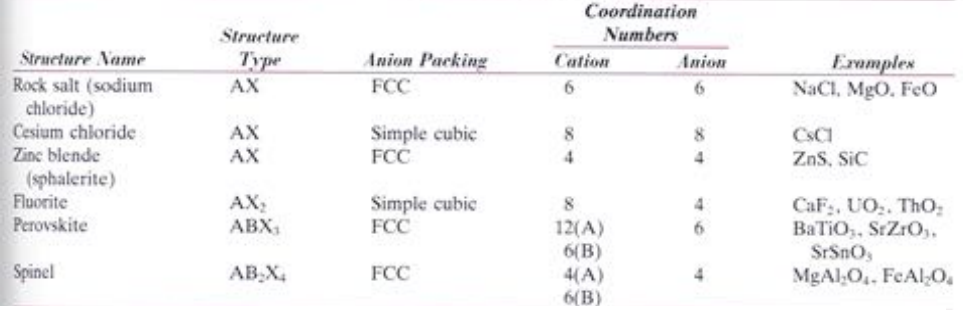


NaCl: large

CaF_2: large

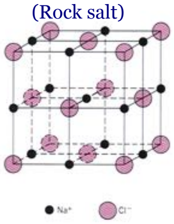
SiC: small

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
H 2.1																	He –
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne –
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar –
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr –
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe –
Cs 0.7	Ba 0.9	La–Lu 1.1–1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn –
Fr 0.7	Ra 0.9	Ac–No 1.1–1.7															

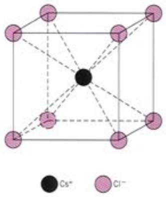


Structure Name	Structure Type	Anion Packing	Coordination Numbers		Examples
			Cation	Anion	
Rock salt (sodium chloride)	AX	FCC	6	6	NaCl, MgO, FeO
Cesium chloride	AX	Simple cubic	8	8	CsCl
Zinc blende (sphalerite)	AX	FCC	4	4	ZnS, SiC
Fluorite	AX_2	Simple cubic	8	4	CaF_2, UO_2, ThO_2
Perovskite	ABX_3	FCC	12(A) 6(B)	6	$BaTiO_3$, $SrZrO_3$, $SrSnO_3$
Spinel	AB_2X_4	FCC	4(A) 6(B)	4	$MgAl_2O_4$, $FeAl_2O_4$

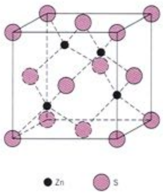
NaCl
(Rock salt)



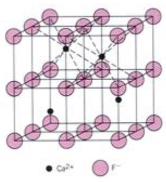
CsCl



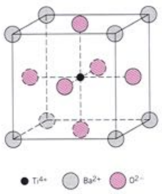
ZnS
(Zinc-blende)



CaF_2
(Fluorite)



$BaTiO_3$
(Perovskite)



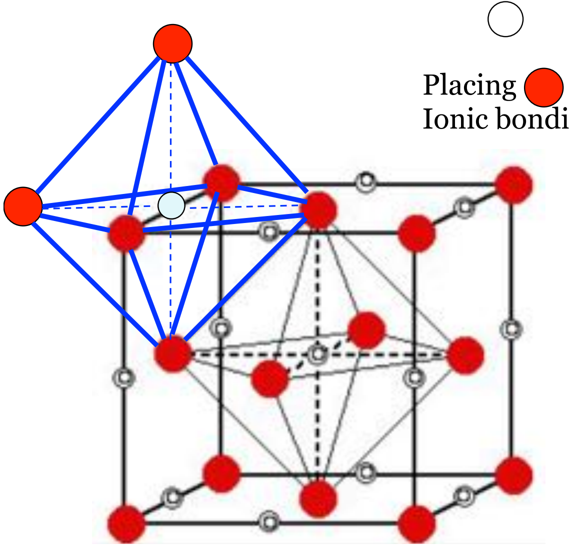
Is there any guide line to predict which structure is taken for a given set of pair ions?

Low EN High EN

$(A)_n(X)_m$

○ ●

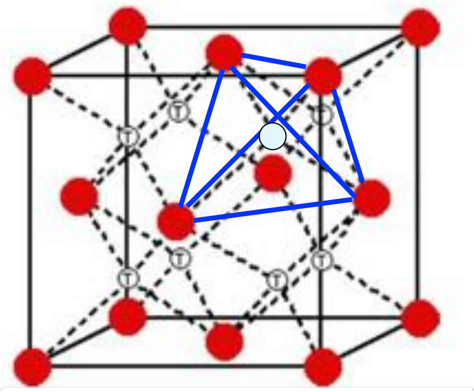
Placing ● in FCC positions
Ionic bonding is omni-directional.



Octahedral interstitial sites

- How many octahedral sites seen?

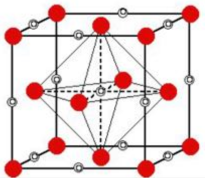
Center= 1 Edge= 12
100% 25%
Total= 1•100% + 12• 25% = 4 sites/cell
Symmetric

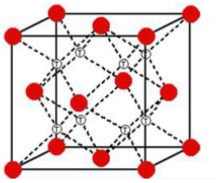


Tetrahedral interstitial sites

- How many tetrahedral sites seen?

Inside =8
100%
Total= 8•100% = 8 sites/cell
Symmetric





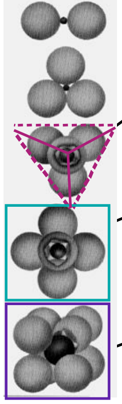
# of Anions X Always=4	Cations M in Oct. sites Max=4	Cations M in Tetra. Sites Max=8	Stoichiometry	Examples
4	4 (100%)	0	M4X4 (MX)	NaCl (6:6 CN)
4	0	8 (100%)	M8X4 (M2X)	K2O Anti-fluoride
4	0	4 (50%)	M4X4 (MX)	ZnS Zincblende
4	2 (50%)	0	M2X4 (MX2)	CaF2 Fluoride
4	4 (100%)	8 (100%)	(M12X4) M3X	So far * Not known
4	2 (50%)	1 (12.5%)	M3X4	MgAl2O4 Spinel

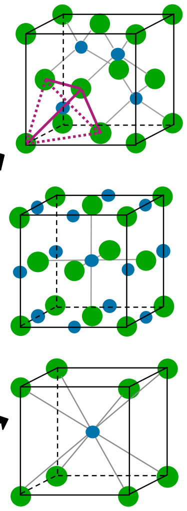
Is there any guide line to predict which structure is taken for a given set of pair ions?

Coordination # and Ionic Radii

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

To form a stable structure, how many anions can surround a cation?

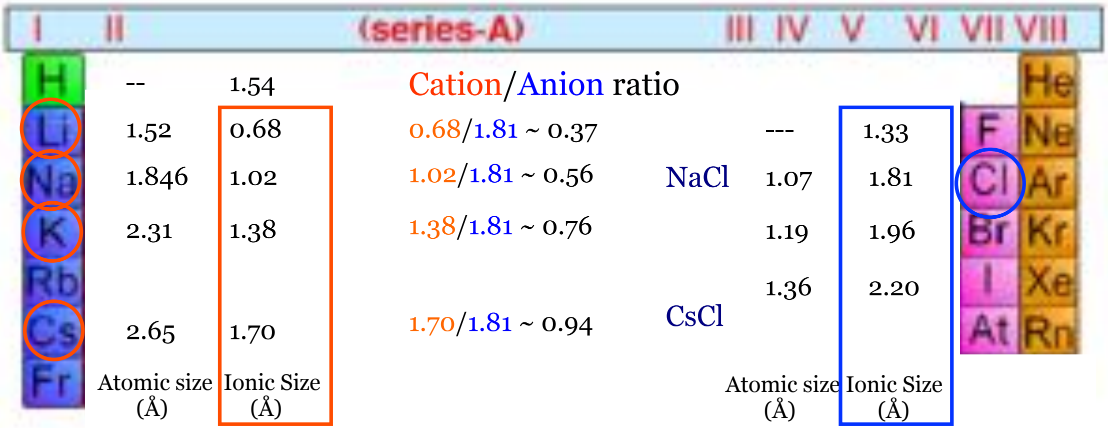
$\frac{r_{cation}}{r_{anion}}$	Coord #		
< 0.155	2	linear	
0.155 - 0.225	3	triangular	
0.225 - 0.414	4	tetrahedral	
0.414 - 0.732	6	octahedral	
0.732 - 1.0	8	cubic	



ZnS
(zinc blende)

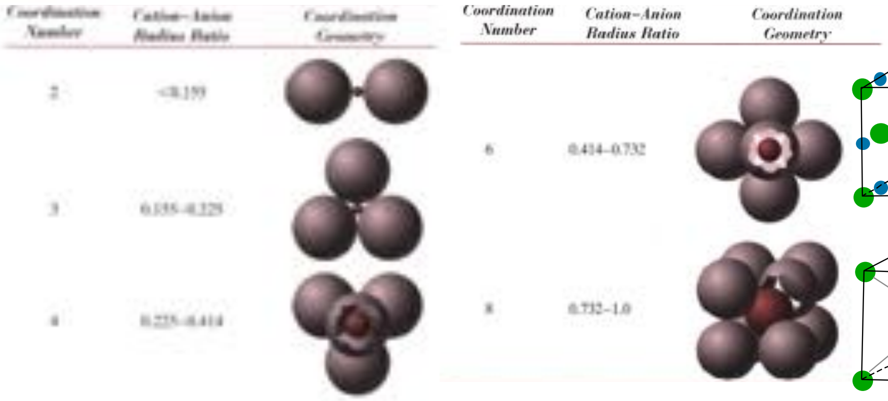
NaCl
(sodium
chloride)

CsCl
(cesium
chloride)

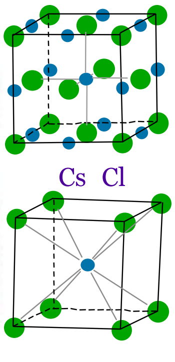


			Cation/Anion ratio				
H	--	1.54					He
Li	1.52	0.68	0.68/1.81 ~ 0.37		---	1.33	F Ne
Na	1.846	1.02	1.02/1.81 ~ 0.56	NaCl	1.07	1.81	Cl Ar
K	2.31	1.38	1.38/1.81 ~ 0.76		1.19	1.96	Br Kr
Rb					1.36	2.20	I Xe
Cs	2.65	1.70	1.70/1.81 ~ 0.94	CsCl			At Rn
Fr	Atomic size (Å)	Ionic Size (Å)			Atomic size (Å)	Ionic Size (Å)	
		Cation				Anion	

$\frac{r_{cation}}{r_{anion}}$



Coordination Number	Cation–Anion Radius Ratio	Coordination Geometry
2	<0.155	
3	0.155–0.225	
4	0.225–0.414	
6	0.414–0.732	
8	0.732–1.0	



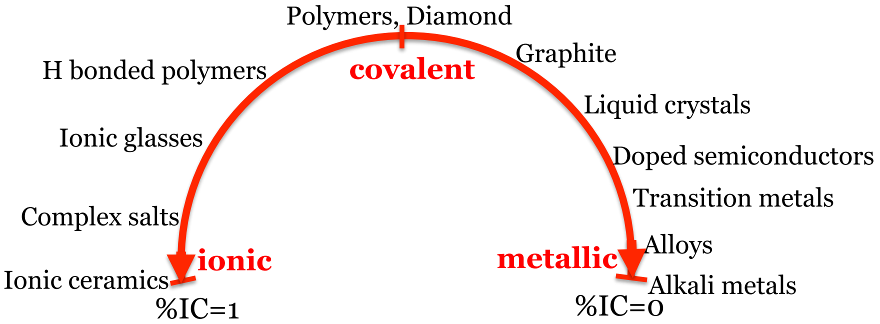
[III]
MATERIALS AND BONDING:
Metallic, Covalent and Ionic characters

- What promotes metallic bonding?
- What properties are inferred from metallic bonding?
- Basis of the electronic structure of metals

UW courses
Background MSE 170 (Callister: Chapter 2, 12, 14)
General Chemistry 100 level
General Physics 100 level

UG course MSE 351 Grad courses MSE 510, MSE 518

[I]. Nature of the Bond and Band Formation


Polymers, Diamond
H bonded polymers
covalent
Graphite
Liquid crystals
Ionic glasses
Doped semiconductors
Transition metals
Complex salts
ionic
metallic
Alloys
Ionic ceramics
Alkali metals
%IC=1
%IC=0

Ionic
- Exchange of valence electrons
- Electrostatic (culombic) attractive forces
- Non-directional nature (favor high symmetric str with high CN#)
- Large bonding energies

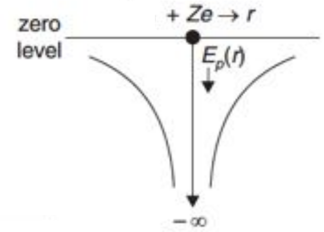
Covalent
- Shared electrons between adjacent atoms
- Directional nature (favor low CN#)
- Wide range of bonding energies

Metallic
- Electron cloud / ion core
- Delocalized nature
- Wide range of bonding energies

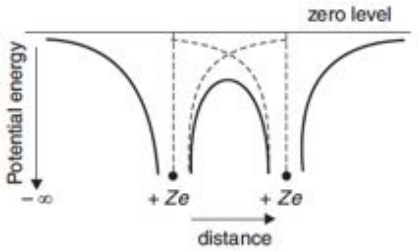
General Treatment of Energy Bands in X'tal

- A **crystal** is a solid consisting of a regular and repetitive arrangement of atoms, ions or molecules in space.
- Positions of the atoms in the crystal are **lattice points**, forming a **crystal lattice**.
- The distance between the atoms in a crystal is fixed and is termed as **lattice constant**.

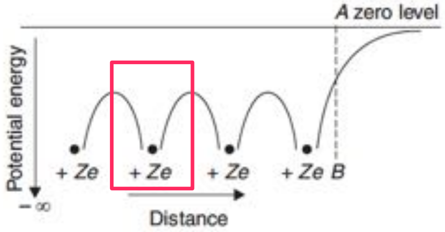
Variation of potential energy of an e⁻ with its distance from the nucleus.



Potential energy variation of an e- with distance between two identical nuclei



Potential energy variation of an e- along a row of atoms in a crystal



Apply Schrodinger equation

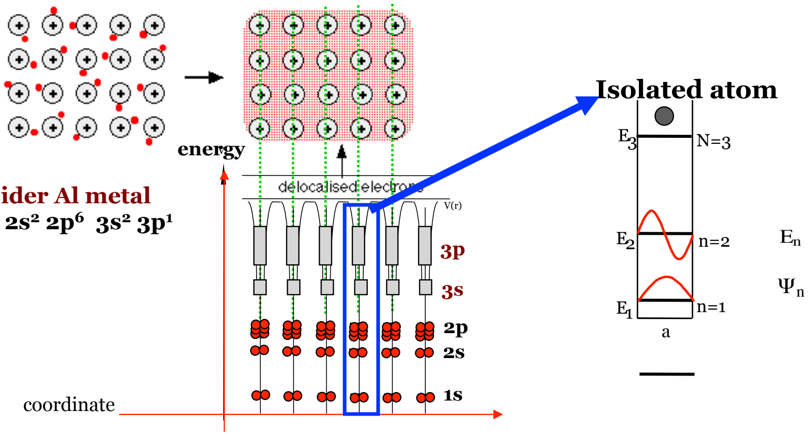
$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \boxed{V(x)}\psi = E\psi$$

$$\hat{H}\psi = E\psi$$

An intuitive idea of "Atom Bonding"

Consider Al metal

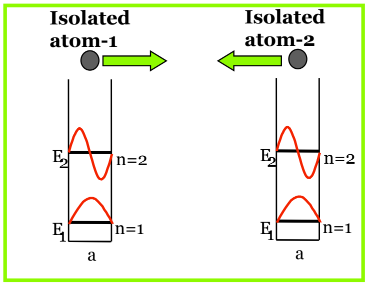
Al=1s² 2s² 2p⁶ 3s² 3p¹



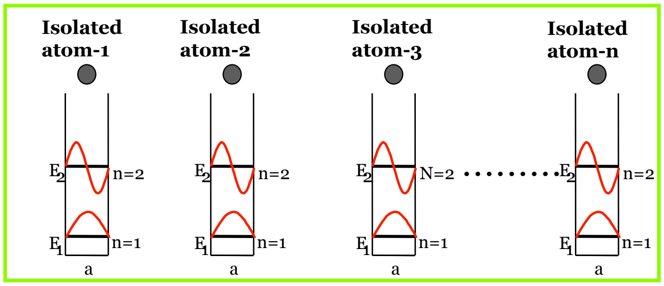
$$E_n = \frac{h^2}{2m}\left(\frac{\pi}{a}\right)^2$$

$$\Psi_n = \sqrt{\frac{2}{a}}\, i \sin\left(\frac{2\pi}{a}x\right)$$

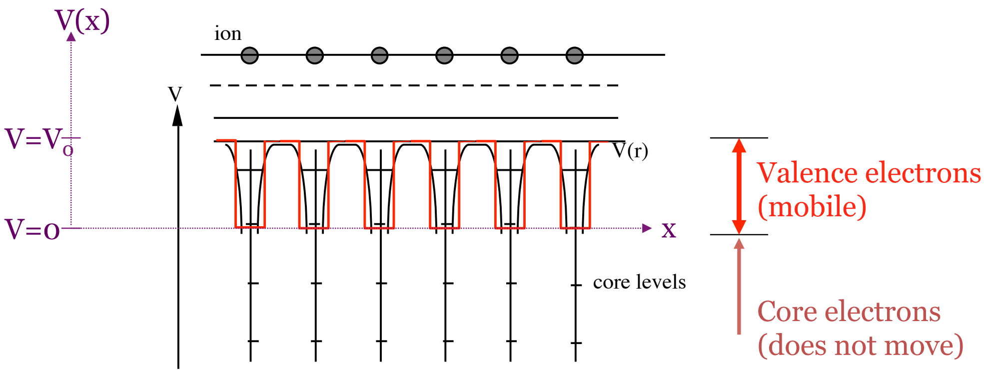
Consider: Bring two atoms from the distance



Then, bring many atoms from the distance

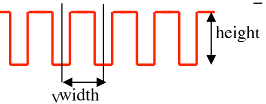


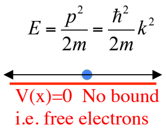
Electrons in the Periodic Potential
A Next Level Approach : The Kronig-Penney Model



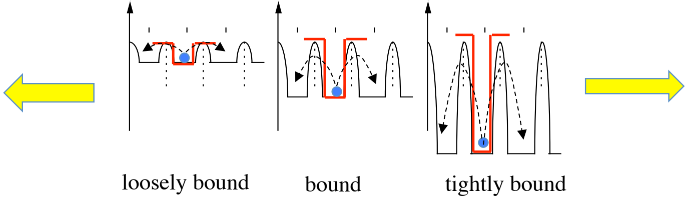
Schrodinger equation
$$\frac{\partial^2\Psi(x)}{\partial x^2} + \left(\frac{2m}{\hbar^2}(E - \boxed{V(x)})\right)\Psi(x) = 0$$

Approximation of V(x)

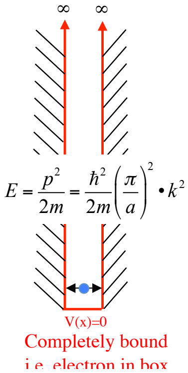



$$E = \frac{p^2}{2m} = \frac{\hbar^2}{2m}k^2$$

V(x)=0 No bound
i.e. free electrons

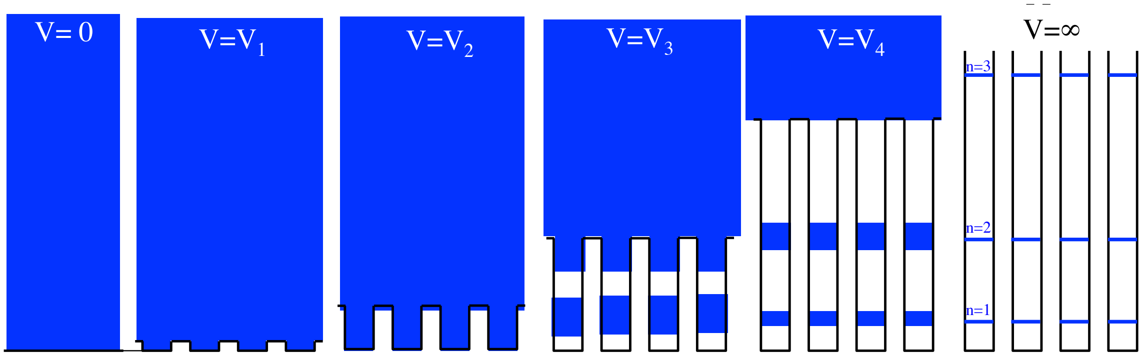


loosely bound bound tightly bound



$$E = \frac{p^2}{2m} = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2 \cdot k^2$$

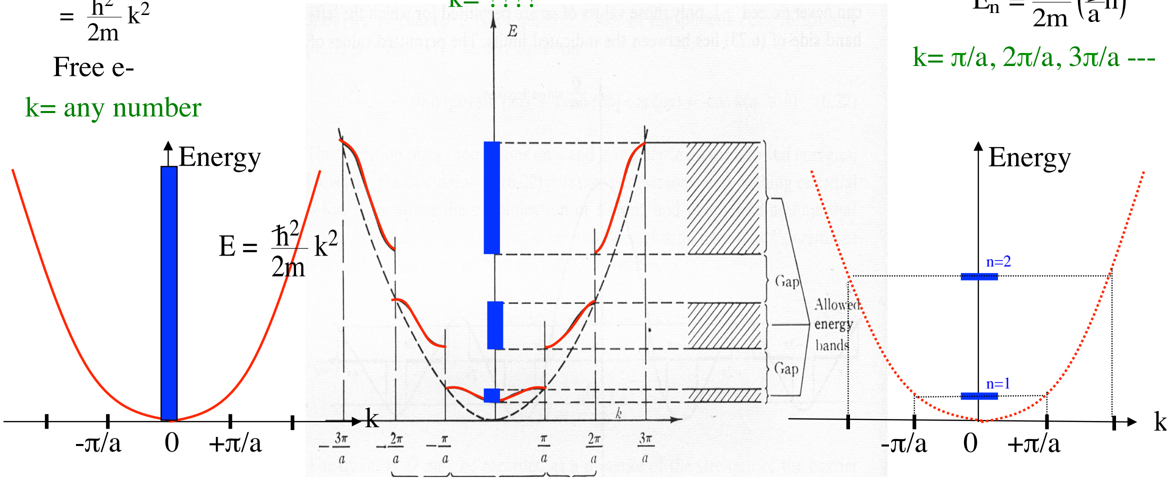
V(x)=0
Completely bound
i.e. electron in box



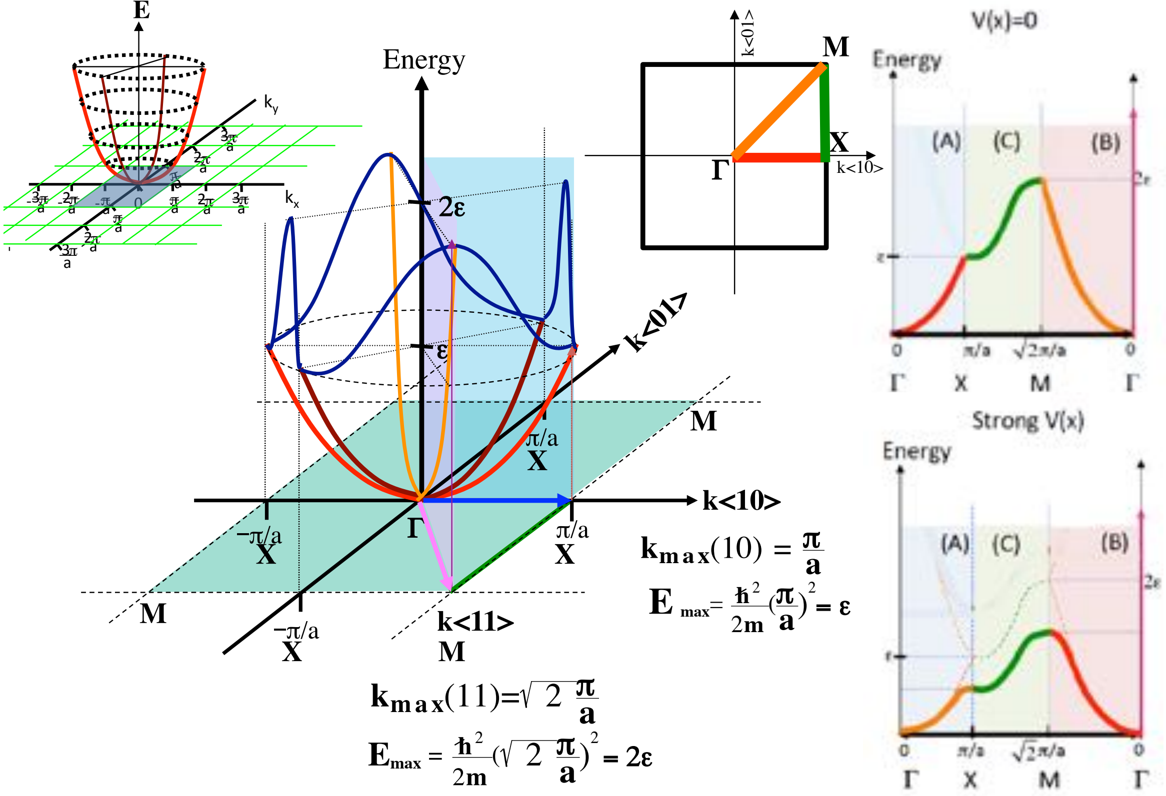
E =contineous
$$= \frac{h^2}{2m}k^2$$
Free e-
k= any number

k= ????

$$E_n = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}n\right)^2$$
k= π/a, 2π/a, 3π/a ---



More accurately illustrated



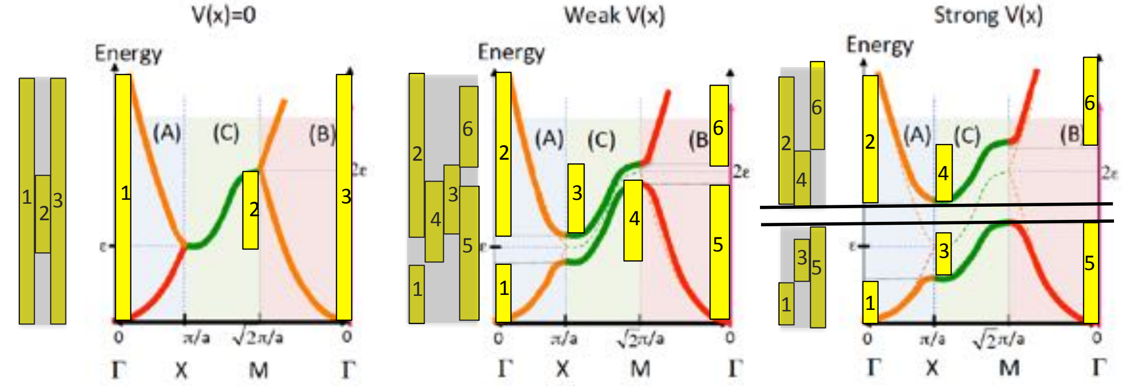
$$k_{max}(10) = \frac{\pi}{a}$$

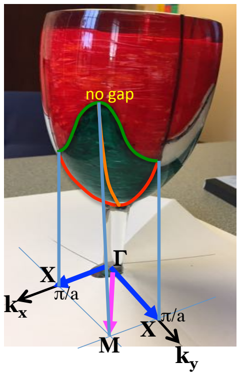
$$E_{max} = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2 = \varepsilon$$

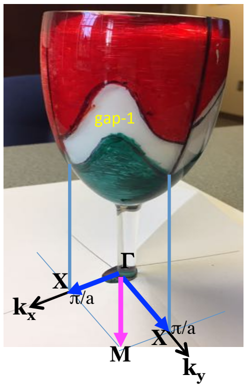
$$k_{max}(11) = \sqrt{2}\,\frac{\pi}{a}$$

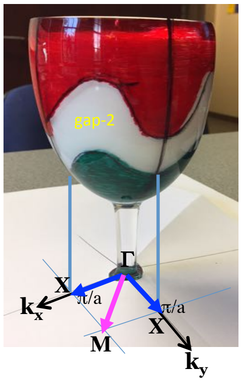
$$E_{max} = \frac{\hbar^2}{2m}\left(\sqrt{2}\,\frac{\pi}{a}\right)^2 = 2\varepsilon$$

[II].Consequence of the Band Formation



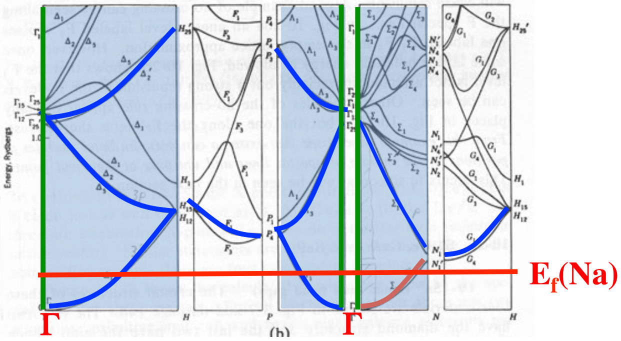




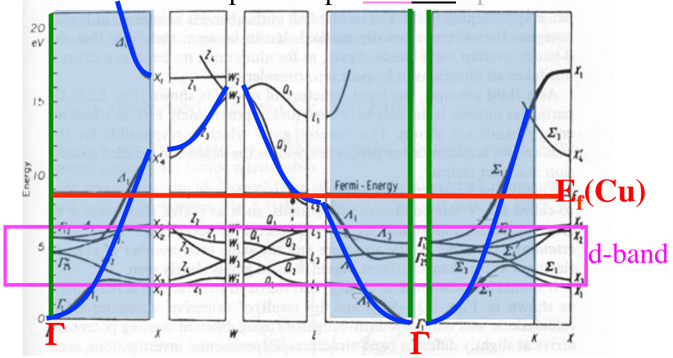


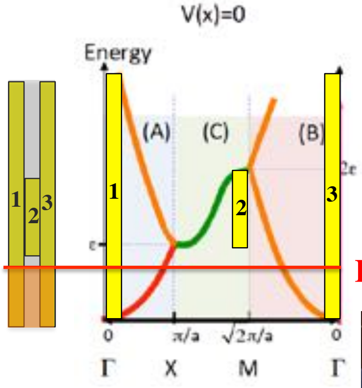
Example(1): Group IA, IB metals

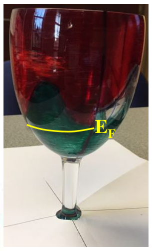
Na: $1s^2\ 2s^2\ 2p^6\ \underline{3s^1}$ 3p 3d 4s---

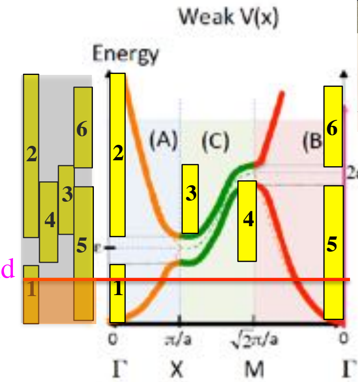


Cu: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \underline{3d^{10}}\ \underline{4s^1}$ 4p 4d 5s---

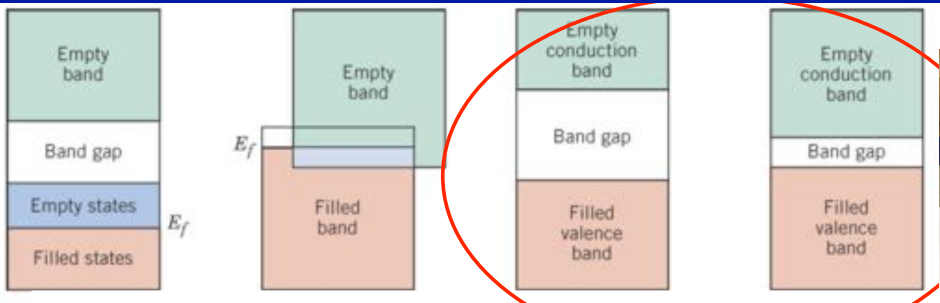




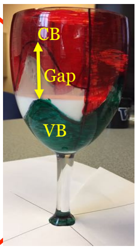




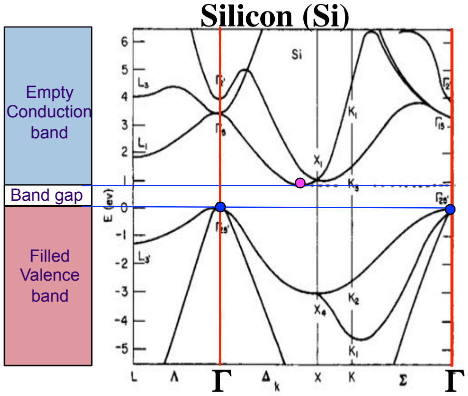
Examples (4): Semiconducting and Insulating Materials



Metals Semimetals Insulators Semiconductors

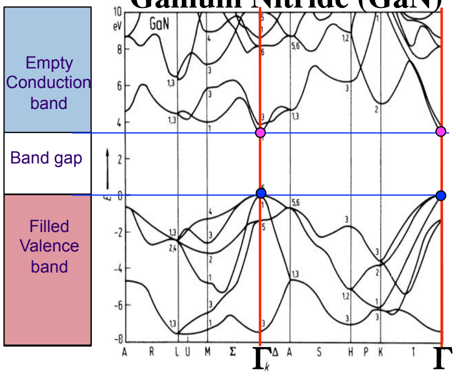


Silicon (Si)

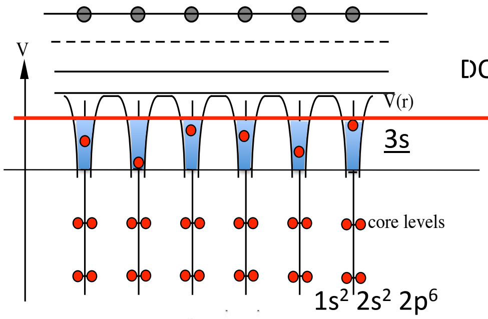


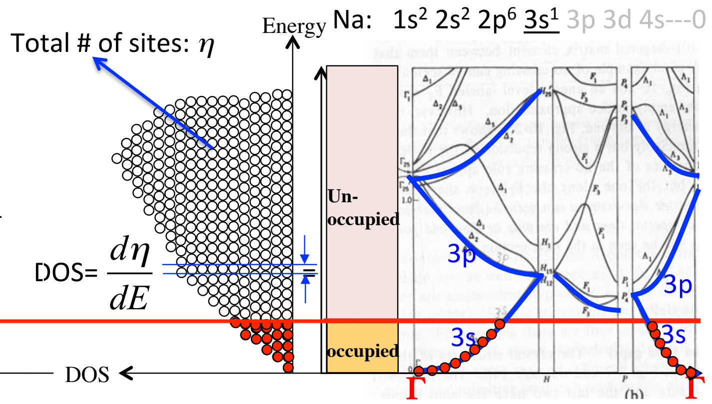
In-direct band gap SC

Gallium Nitride (GaN)



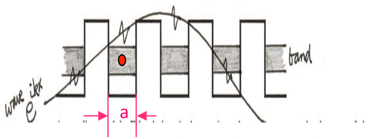
Direct band gap SC




Total # of sites: η

Energy Na: $1s^2\,2s^2\,2p^6\,3s^1$ 3p 3d 4s---0

$$\text{DOS}=\frac{d\eta}{dE}$$



Uncertainty of e^- location (Δx) ≈ a

Heisenberg's uncertainty principle

$$\Delta x \bullet \Delta p \sim h$$

Uncertainty of momentum in

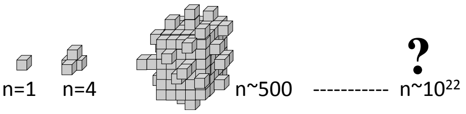
x-direction: $\Delta p_x \sim h/a$

y-direction: $\Delta p_y \sim h/a$

x-direction: $\Delta p_z \sim h/a$

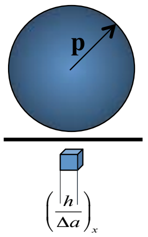
The uncertainty in the momentum per e^-

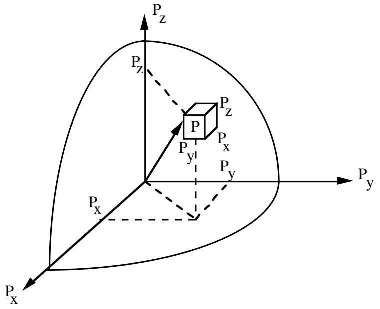
How many e^-? $\sim 10^{22}$ e^-/cm^3



Sup-R. PART[III] 2-3

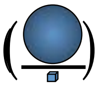
$$\eta=\frac{\text{Volumne of "momentum sphere"}}{\text{momentum element}}=$$





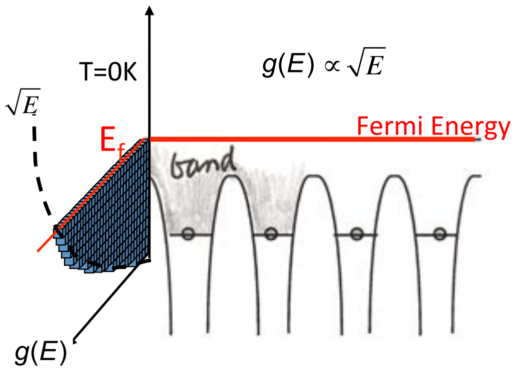
Density of States (DOS) : *g(E)*

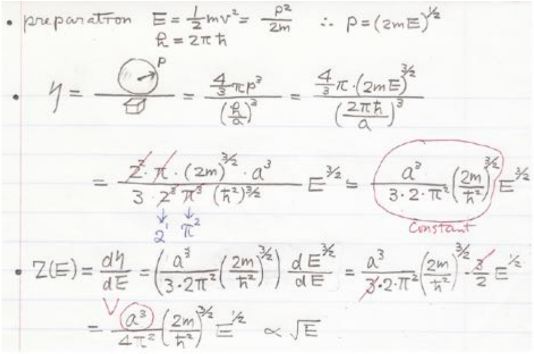
\# of events "per" energy



$$g(E)=\frac{d\eta}{dE}=\frac{d}{dE}\left(\quad\right)$$

$$=\frac{a^3}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\bullet E^{1/2}=\frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\bullet E^{1/2}$$





- preparation $E=\frac{1}{2}mv^2=\frac{p^2}{2m}$ $\therefore p=(2mE)^{1/2}$
  $h=2\pi\hbar$
- $\eta=\frac{\quad}{\quad}=\frac{\frac{4}{3}\pi p^3}{\left(\frac{h}{a}\right)^3}=\frac{\frac{4}{3}\pi\cdot(2mE)^{3/2}}{\left(\frac{2\pi\hbar}{a}\right)^3}$

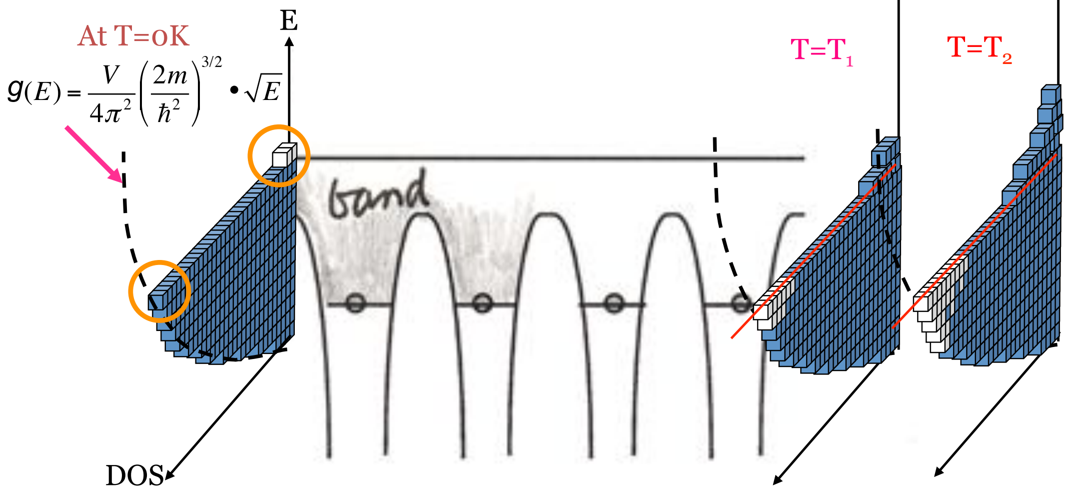
  $$=\frac{\cancel{2}^{2}\cdot\cancel{\pi}\cdot(2m)^{3/2}\cdot a^3}{3\cdot 2^3\pi^3\,(\hbar^2)^{3/2}}E^{3/2}\doteq\boxed{\frac{a^3}{3\cdot2\cdot\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}}E^{3/2}$$

  $\downarrow$ 2^1 $\downarrow$ π^2

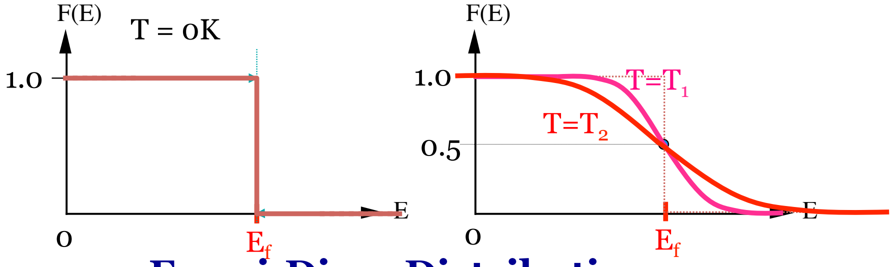
  Constant
- $Z(E)=\frac{d\eta}{dE}=\left(\frac{a^3}{3\cdot2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\right)\frac{dE^{3/2}}{dE}=\frac{a^3}{\cancel{3}\cdot2\cdot\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\cdot\frac{\cancel{3}}{2}E^{1/2}$

  $$=\frac{\overset{V}{\boxed{a^3}}}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}E^{1/2}\propto\sqrt{E}$$

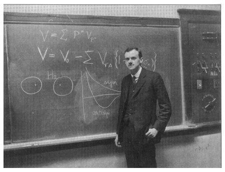
Temperature effect in e-occupation



$$g(E) = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \cdot \sqrt{E}$$

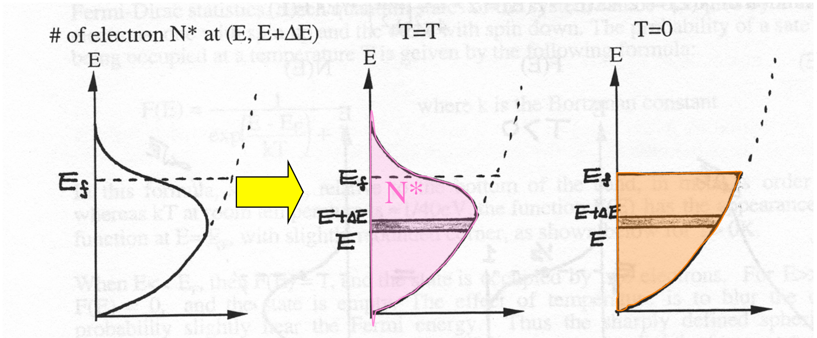


Fermi-Dirac Distribution



Paul Adrien Mourice Dirac (1902-1984) received the Nobel Prize 1933 (sheared With Driwin Schrodinger).

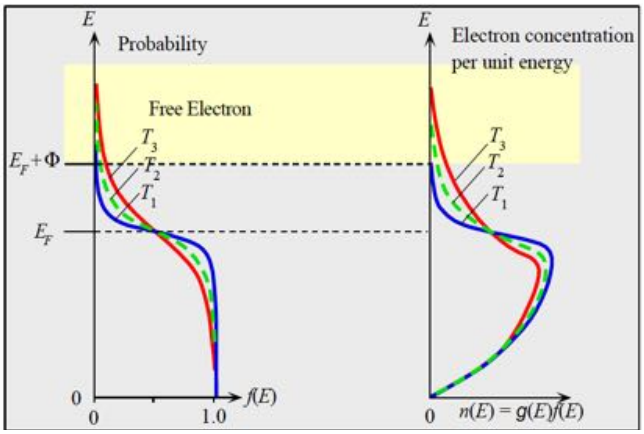
The Fermi Energy



$$N^* = \int N(E)dE$$

$$= \int_0^\infty 2 \cdot g(E) \cdot F(E)\,dE$$

$$= \int_0^{E_F} 2 \cdot g(E) \cdot 1\,dE$$



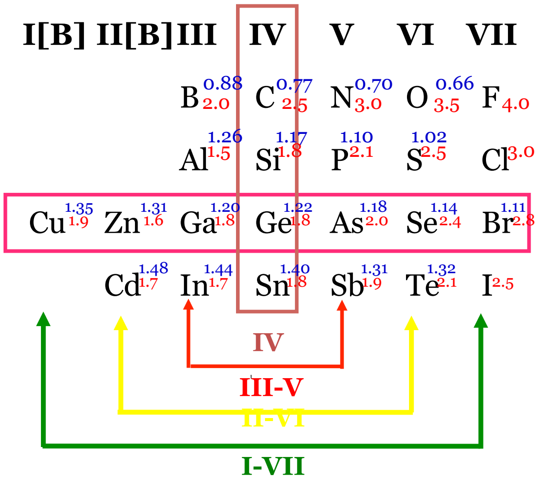
Solve for the Fermi-energy

$$E_F = (3\pi^2 N')^{2/3} \cdot \frac{\hbar^2}{2m}$$

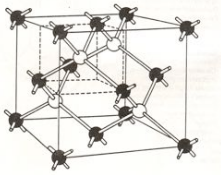
$$N' = \frac{N^*}{V} = \frac{Max\#of.electron}{Volumn}$$

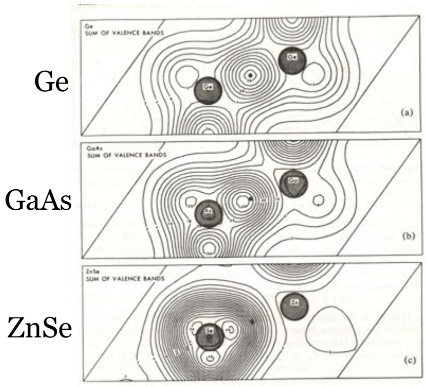
$$= \#of.electron/unit.volume$$

HETEROPOLAR BONDING MATERIALS



I[B]	II[B]	III	IV	V	VI	VII
		B$^{0.88}_{2.0}$	C$^{0.77}_{2.5}$	N$^{0.70}_{3.0}$	O$^{0.66}_{3.5}$	F$_{4.0}$
		Al$^{1.26}_{1.5}$	Si$^{1.17}_{1.8}$	P$^{1.10}_{2.1}$	S$^{1.02}_{2.5}$	Cl$^{3.0}$
Cu$^{1.35}_{1.9}$	Zn$^{1.31}_{1.6}$	Ga$^{1.20}_{1.8}$	Ge$^{1.22}_{1.8}$	As$^{1.18}_{2.0}$	Se$^{1.14}_{2.4}$	Br$^{1.11}_{2.8}$
	Cd$^{1.48}_{1.7}$	In$^{1.44}_{1.7}$	Sn$^{1.40}_{1.8}$	Sb$^{1.31}_{1.9}$	Te$^{1.32}_{2.1}$	I$^{2.5}$

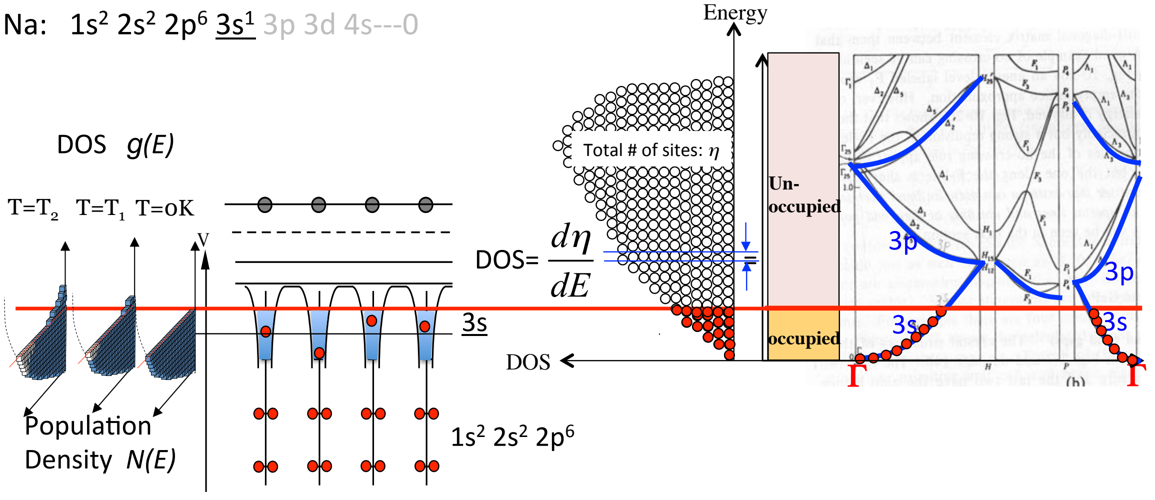




Ge	GaAs	ZnSe	CuBr	
[IV]	[III-V]	[II-VI]	[I-VII]	(isoelectric system)
Diamond	Zinc-Blende	Zinc-Blende	Rock-Salt	
1.22+1.22 =2.44	1.26+1.18 =2.44	1.31+1.14 =2.45	1.35+1.11 =2.46	(Å) Interatomic distance
1.8-1.8 =0.0	2.0-1.8 =0.2	2.4-1.6 =0.8	2.8-1.9 =0.9	Electronegativity

Covaleznt ⟷ Ionic

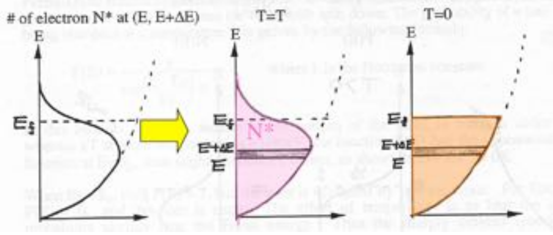
Na: $1s^2\ 2s^2\ 2p^6\ \underline{3s^1}$ 3p 3d 4s---0



$$N(E)=\overset{\text{spin degenracy}}{2}\bullet\underset{\text{DOS}}{g(E)}\bullet\overset{\text{F-D function}}{F(E)}=2\bullet\frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E}\bullet F(E)$$

Fermi-Dirac distribution function

$$F(E)=\frac{1}{\exp\left(\frac{E-E_F}{kT}\right)+1}$$



$$N^*=\int N(E)dE$$
$$=\int_0^{\infty}2\bullet g(E)\bullet F(E)dE$$
$$=\int_0^{E_F}2\bullet g(E)\bullet 1dE$$

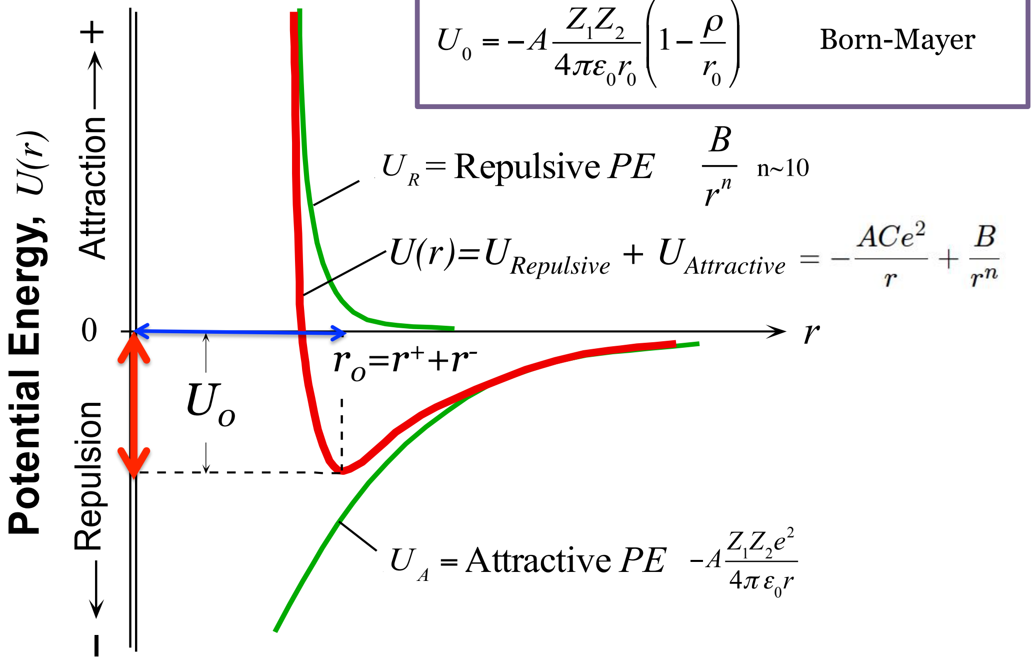
$$E_F=(3\pi^2N')^{2/3}\bullet\frac{\hbar^2}{2m}$$

$$N'=\frac{N^*}{V}=\frac{Max\#of.electron}{Volumn}$$
$$=\#of.electron/unit.volume$$

Potential Energy of an Ion Pair

$$U_0 = -A\frac{Z_1Z_2}{4\pi\varepsilon_0 r_0}\left(1-\frac{1}{n}\right)$$ Born-Lande

$$U_0 = -A\frac{Z_1Z_2}{4\pi\varepsilon_0 r_0}\left(1-\frac{\rho}{r_0}\right)$$ Born-Mayer



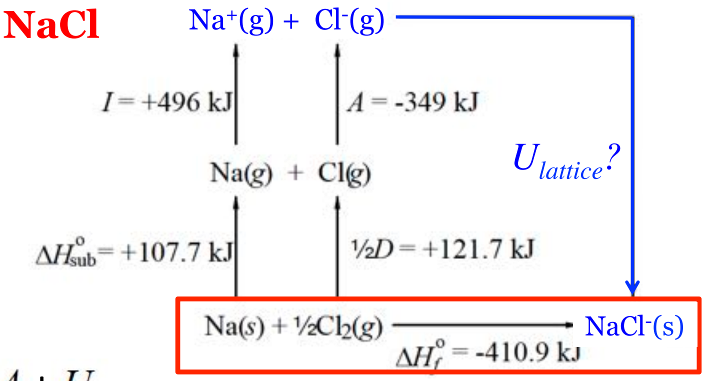
- Lattice energy, $U_{lattice}$, is defined as the enthalpy required to form one mole of crystalline solid in its standard state from the gaseous ions

Example: $Na^+(g) + Cl^-(g) \longrightarrow NaCl(s)$ $\boxed{U_{lattice} = -786.8\text{kJ/mole}}$

This reaction is *exothermic* (spontaneously happen) Want to know

- How do you find $U_{lattice}$?

Born-Haber Cycle for NaCl



Thermodynamics data (per mole)

$Na(s) \rightarrow Na(g)$	$\Delta H^o_{sub} = 107.7$ kJ
$Na(g) \rightarrow Na^+(g) + e^-$	$I = 496$ kJ
$½Cl_2(g) \rightarrow Cl(g)$	$½D = 121.7$ kJ
$Cl(g) + e^- \rightarrow Cl^-(g)$	$A = -349$ kJ
$Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$	$U_{lattice}$=?
$Na(s) + ½Cl_2(g) \rightarrow NaCl(s)$	$\Delta H^o_f = -410.9$ kJ

$$\Delta H^o_f = \Delta H^o_{sub} + I + ½D + A + U_{lattice}$$

$$U_{lattice} = -(\Delta H^o_{sub} + I + ½D + A) + \Delta H^o_f$$
$$= -(107.7\text{ kJ} + 496\text{ kJ} + 121.7\text{ kJ} + (-349\text{ kJ}) + (-410.9)\text{kJ})$$
$$= \boxed{-787\text{ kJ/mole}}$$

[IV]
MATERIAL’S FUNDAMENTAL PROPERTIES

A Volume-Based Thermodynamics (VBT) approach

- Introduction of volume-based thermodynamics approach
- Formula unit volume and mean average bonding volume
- Significance of the lattice energy
- Material’s fundamental properties inferred from the lattice energy

Background	MSE 170 (Callister: Chapter 2, 12, 14)	
	General Chemistry 100/200 level	
	General Physics 100/200 level	
UG courses	MSE 322	MSE 351
Grad courses	MSE 510	MSE 560

VOLUME-BASED THERMODYNAMICS (VBT) APPROACH
“Predictive Thermodynamics for Condensed Phases”

- For hypothetical materials or materials under development, experimental data are often unavailable, or necessarily impossible to obtain.

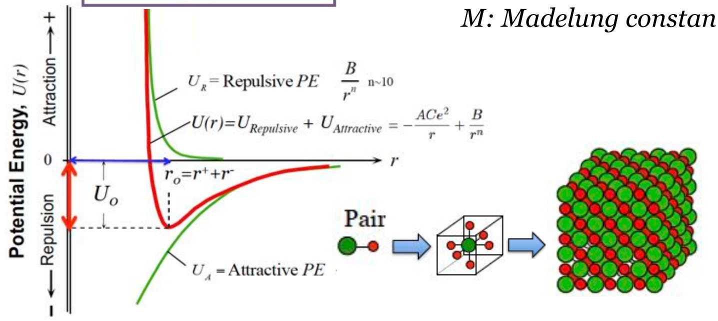
- *Modulus of elasticity*, *thermal expansion coefficient*, *melting temperature* *are three material’s fundamental properties directly inferred from the lattice energy of the* condensed phases.

$$U_0 = -A\frac{Z_1Z_2}{4\pi\varepsilon_0 r_0}\left(1-\frac{1}{n}\right) \quad \text{Born-Lande}$$

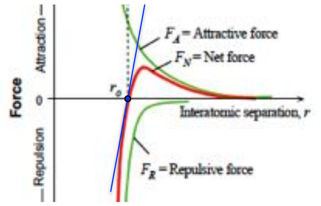
$$U_0 = -A\frac{Z_1Z_2}{4\pi\varepsilon_0 r_0}\left(1-\frac{\rho}{r_0}\right) \quad \text{Born-Mayer}$$

$$\Rightarrow \quad U_{lattice} = M \bullet U_o$$

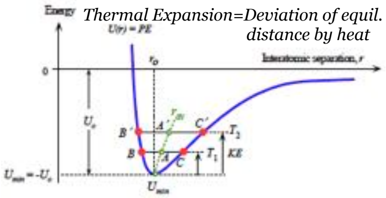
M: Madelung constant



Modulus of Elasticity =Slope of force curve



Thermal Expansion=Deviation of equil. distance by heat



- Original work done by Classer and Jenkins* is a method applied to both ionic and covalent solids, principally via “*formula unit volumes*”, providing a new thermo-dynamic tool for such assessment.

Procedure

(1) **Formula unit (fU) volume (V_m)**

$$V_m = \frac{W_m}{\rho}$$

W_m: Formula weight of material
ρ : Density of material

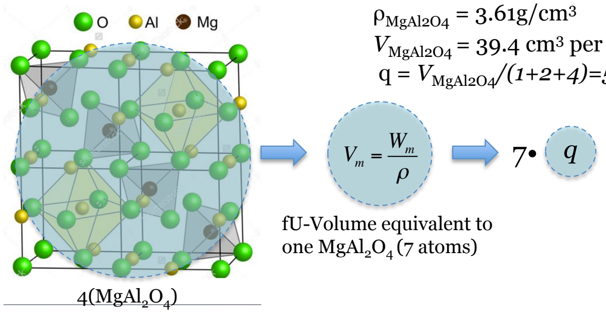
(2) **Mean average bonding volume (q)**

$$q = \frac{V_m}{N_m}$$

V_m: Formula unit volume (fU)
N_m: # of atoms (in 1-fU)

Example: $MgAl_2O_4$ (Spinel)

$W_{MgAl2O4}$= 142.27g/mole
$\rho_{MgAl2O4}$ = 3.61g/cm^3
$V_{MgAl2O4}$ = 39.4 cm^3 per mole
q = $V_{MgAl2O4}/(1+2+4)=5.6$ (cm^3/fU-atom)



fU-Volume equivalent to one $MgAl_2O_4$ (7 atoms)

Mean average "bonding volume" of atom in 1-fU of material.

Summary of q values of various materials

(1) A "q" value varies from material to material, but many materials show **q~6.5 cm^3/atom-fU** (i.e., per atom in 1-fU of material) except a few cases.

(2) This means: Mean bonding volume of atom in 1-fU of the material (unit:cm^3/atom-fU) is similar for all materials.

(3) Material specific values of "q".

Multivalent Oxides	q~6.5-7.5cm^3/atom-fU
Monovalent Oxides	q~11.5cm^3/atom-fU
Nitrides	q~6.5 cm^3/atom-fU
Carbides	q~6.5 cm^3/atom-fU
Fluorides	q~7.4±1.2(20%) cm^3/atom-fU
Hydro-oxides	q~9.1±1.2(13%) cm^3/atom-fU
Chlorides	q~13.3±1.8(14%) cm^3/atom-fU

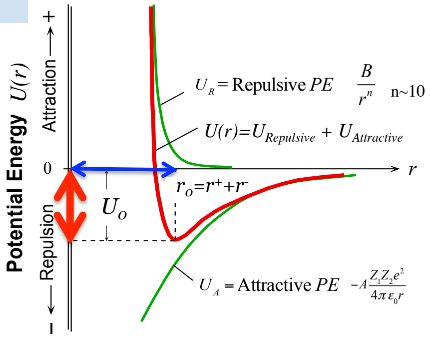
$(A)_n(B)_m$

(4) Material's properties (such as E, α, C_p etc) can be expressed in terms of q. (to be discussed in later chapters)

[II]. LATTICE ENERGY, $U_{lattice}$

Recent progress on estimating $U_{lattice}$ from V_m and ionic separation

Three recent papers
1. Jenkins, et al., Inorganic Chemistry 1999, **38**, 3609-3620.
2. Glasser, et al., J. Am. Chem. Soc. 2000, **122**, 632-638.
3. Kaya and Kaya, Inorganic Chemistry 2015, **54**(17), 8207-8213.



Summary of three papers:

(1). Started with either Born-Lande or Kapustinskii's equation for lattice energy.

$$U_{lattice}=-A\frac{MZ_1Z_2}{4\pi\varepsilon_0 r_0}\left(1-\frac{1}{n}\right)$$

$$U_{lattice}=-\frac{1.202\bullet 10^5 \nu Z_1Z_2}{r^++r^-}\left(1-\frac{34.5}{r^++r^-}\right)$$

(2). Parameterized the equation in a form of:

$$U_{lattice}=2I\left[\frac{\alpha}{V_m^{1/3}}+\beta\right]$$ where α and β are empirical consts

(3). Ionic separation <r> is evaluated through formula volume (V_m) as $\langle r\rangle=(V_m)^{1/3}/2$

(4). Introduction of "*chemical hardness*" (ref. 3), then developed parameterized equation in a form of:

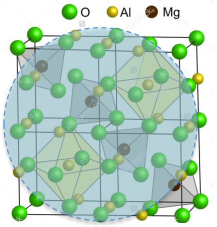
$$U_{lattice}=2I\left[a\frac{\eta_M}{V_m^{1/3}}+b\right]$$

This form can be applied to materials with $U_{lattice}$<5000kJ/mole very accurately.

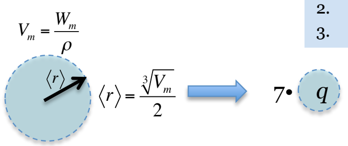
Estimation of $U_{lattice}$ from V_m and ionic separation

Example: $MgAl_2O_4$ (Spinel)

Three recent papers
1. Jenkins, et al., Inorganic Chemistry 1999, **38**, 3609-3620.
2. Glasser, et al., J. Am. Chem. Soc. 2000, **122**, 632-638.
3. Kaya and Kaya, Inorganic Chemistry 2015, **54**(17), 8207-8213.



$4(MgAl_2O_4)$



$$V_m=\frac{W_m}{\rho}$$

$$\langle r\rangle=\frac{\sqrt[3]{V_m}}{2}$$

$7\bullet q$

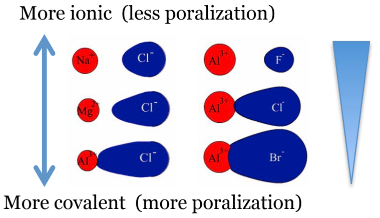
1 fU-Volume equivalent to one $MgAl_2O_4$ (7 atoms)

Mean average "bonding volume" of atom in 1-fU of material.

Born-Lande eq. for $U_{lattice}$ → Parameterized equation for each material

$$U_{lattice}=-A\frac{MZ_1Z_2}{4\pi\varepsilon_0 r_0}\left(1-\frac{1}{n}\right) \rightarrow \underset{\text{(Ref. 1)}}{U_{lattice}}=2I\left[\frac{\alpha}{V_m^{1/3}}+\beta\right] \rightarrow \underset{\text{(Ref. 2)}}{U_{lattice}}=2I\left[a\frac{\eta_M}{V_m^{1/3}}+b\right]$$

η_M= "Chemical hardness" A measure of the resistance toward electron cloud polarization or deformation of chemical species



Higher chemical hardness (η_M) or large η_M value

Lower chemical hardness (η_M) or low η_M value

Examples

η_{AlF}=8.59

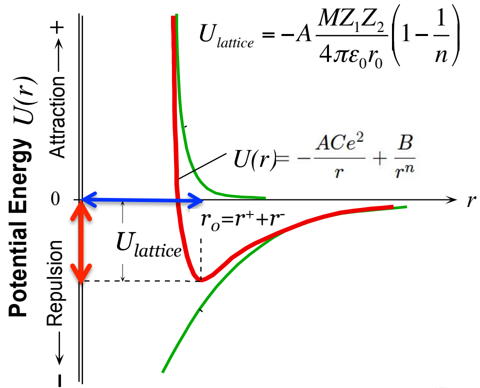
η_{AlCl}=7.35

η_{AlBr}=5.90

(Ref. 2)

Correlation between Lattice energy($U_{lattice}$) & Modulus of Elasticity (E)

(Volume-Based Thermodynamics (VBT) approach)



$$U_{lattice} = -A\frac{MZ_1Z_2}{4\pi\varepsilon_0 r_0}\left(1-\frac{1}{n}\right)$$

$$U(r) = -\frac{ACe^2}{r} + \frac{B}{r^n}$$

At equilibrium position:

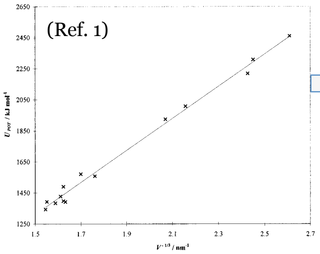
$$(F_{r=ro}) = \left(\frac{dU}{dr}\right)_{r=r_0} = \left(\frac{ACe^2}{r^2} - \frac{nB}{r^{n+1}}\right)_{r=r_0} = 0 \Rightarrow r_o = \left(\frac{nB}{ACe^2}\right)^{\frac{1}{n-1}}$$

Young's modulus: $E = \left.\frac{d\sigma}{d\epsilon}\right|_{\epsilon\to 0} = \left.\frac{1}{r_0}\frac{dF}{dr}\right|_{r\to r_0}$

$$= \left.\frac{1}{r_0}\frac{d}{dr}\left(\frac{ACe^2}{r^2} - \frac{nB}{r^{n+1}}\right)\right|_{r\to r_0}$$

Go through derivation, then you get: $E = \frac{(n-1)ACe^2}{r_0^4}$

Modulus of elasticity: $E = \frac{(n-1)ACe^2}{r_0^4} \propto \frac{1}{(r_0)^4} \equiv \frac{1}{r_0} \bullet \frac{1}{(r_0)^3} \propto \frac{1}{(V_m)^{1/3}} \bullet \frac{1}{V_m} \equiv \frac{U_{lattice}}{V_m}$



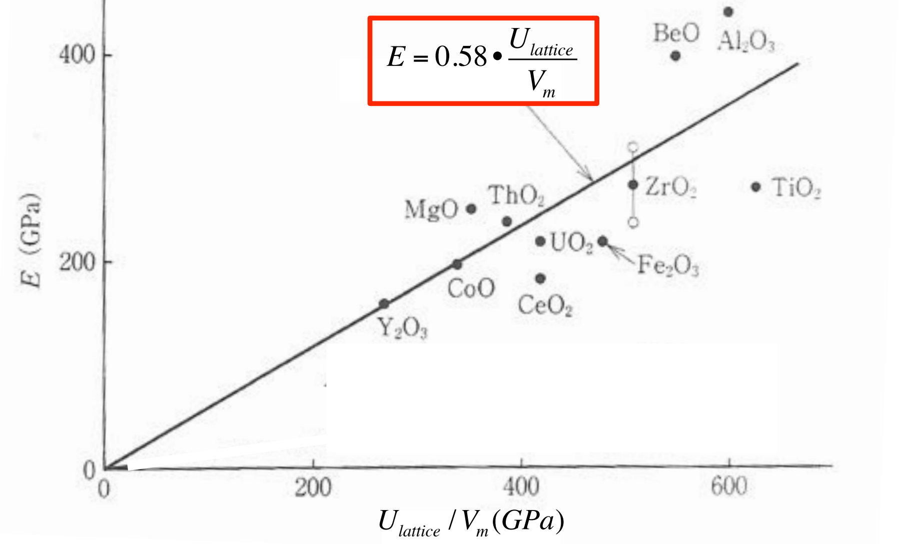
$$\Rightarrow U_{lattice} \propto \frac{1}{(V_m)^{1/3}}$$

$$\therefore\ E = const \bullet \frac{U_{lattice}}{V_m}$$

V_m: Formula unit (fU) volume
N_m: # of atoms in 1-fU.

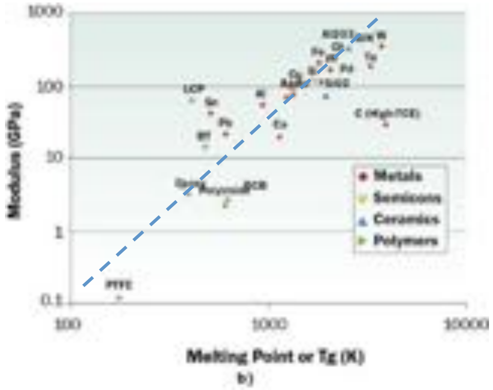
Estimation of the Modulus of Elasticity (E) For Known Materials

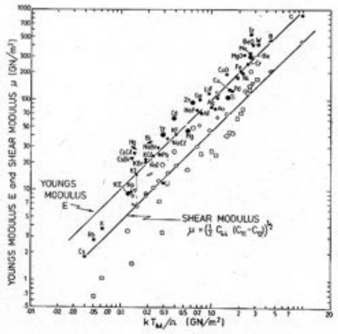
$$E = const \bullet \frac{U_{lattice}}{V_m}$$



If you **know** the material you are working, $U_{lattice}$ and V_m are known.

Experimental facts about *E* vs T_m





- Materials data indicate: $E \propto T_m$ or $E = \zeta T_m$
- *E* and T_m have different dimensions: Dimensional analysis of ζ

$$[\zeta] \equiv \frac{\overset{\text{Young's Modulus}}{[E]}}{\underset{\text{Melting temperature}}{[T_m]}} = \left[\frac{\frac{(force)}{m^2}}{^\circ K}\right] = \left[\frac{\frac{Kg \bullet \frac{m}{\sec^2}}{m^2}}{^\circ K}\right] = \left[\frac{Kg}{m \bullet \sec^2 \bullet ^\circ K}\right] = \left[\frac{\frac{Kg \bullet m^2}{\sec^2}}{m^3 \bullet ^\circ K}\right] \equiv \frac{(energy)}{(volume) \bullet (temp)} \equiv \frac{\overset{C_p}{(heat-capacity)}}{\underset{\text{Formula volume}}{(volume)}}$$

$$E = \zeta T_m \propto \frac{(heat-capacity)}{(volume)} \bullet T_m = \frac{C_p}{V_m} \bullet T_m$$

$$E = \zeta T_m \propto \frac{(heat-capacity)}{(volume)} \bullet T_m = \frac{C_p}{V_m} \bullet T_m$$

$$E = const \bullet \frac{C_p T_m}{V_m} = const \bullet \frac{3NRT_m}{V_m} = const \bullet \frac{3RT_m}{\frac{V_m}{N}} = const \bullet \frac{3RT_m}{q}$$

$$\therefore E \propto \frac{T_m}{q}$$