2020 Fall

Introduction to Materials Science and Engineering

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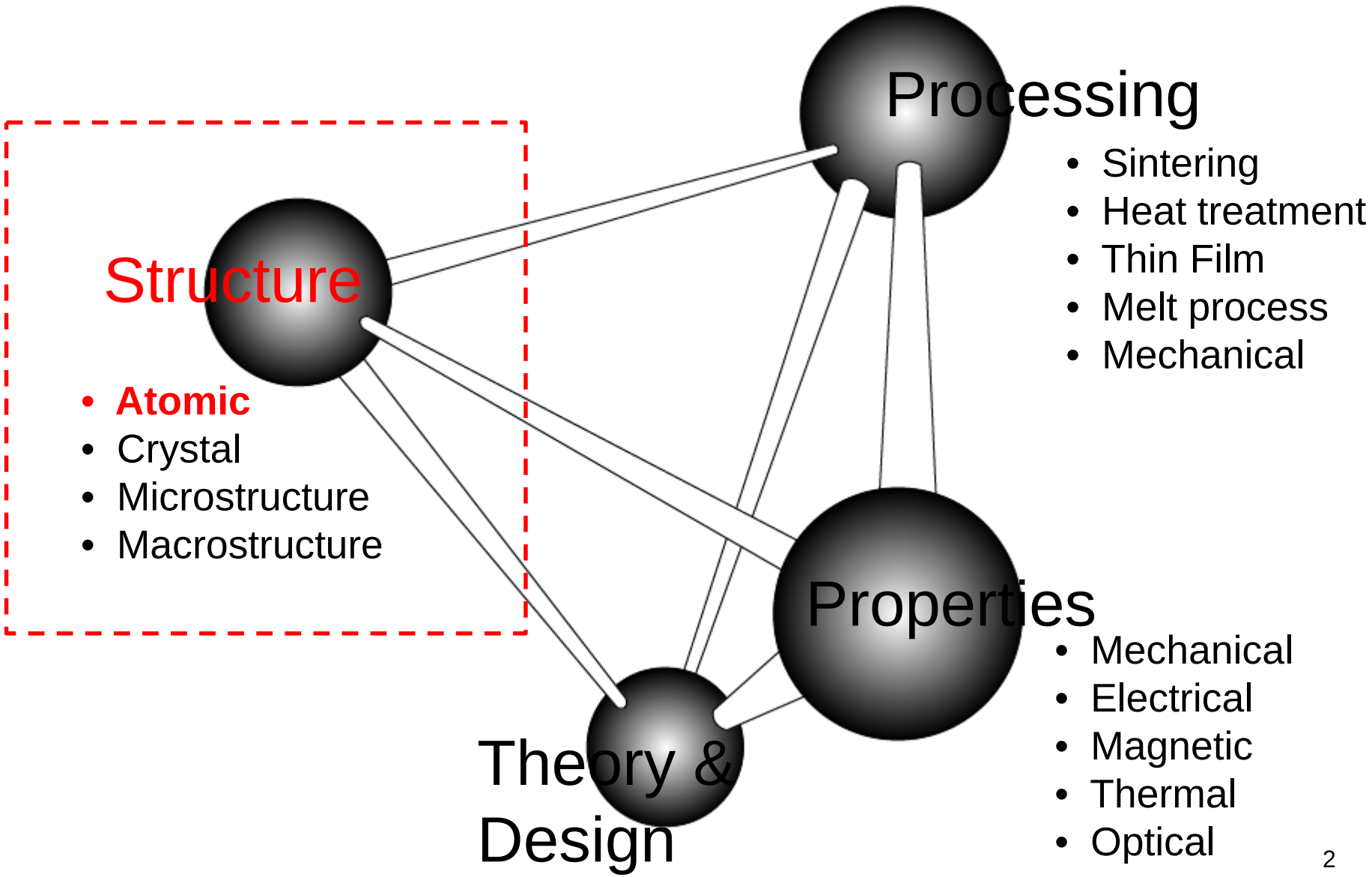
Materials Science and Engineering



CHAPTER 2:
Atomic structure and Interatomic bonding

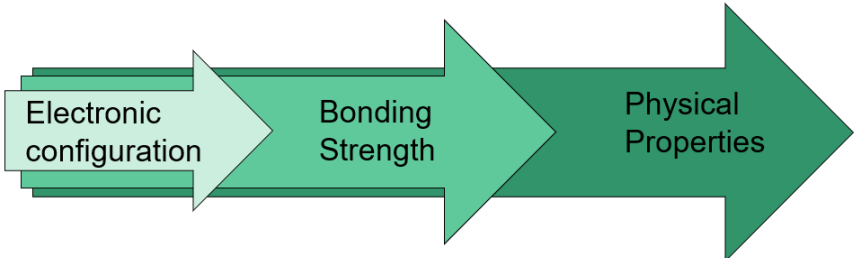
; 많은 경우 결합의 종류로 재료의 특성 설명

ISSUES TO ADDRESS...

- What promotes bonding?
- What types of bonds are there?
- What properties are inferred from bonding?

Contents for previous class

Atomic Structure



2.2 **Fundamental concepts**

- atom – electrons – 9.11×10^{-31} kg
  protons, neutrons } 1.67×10^{-27} kg

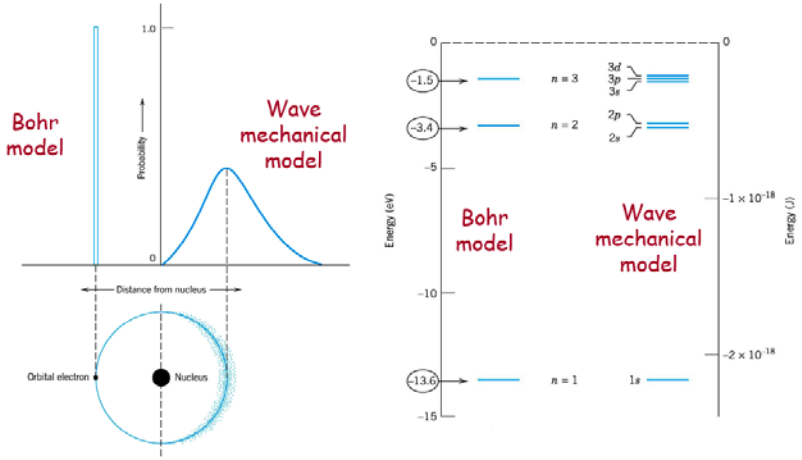
2.3 **Electrons in atoms**

a. atomic models

Bohr's model + Wave-mechanical model

전자는 파동성과 입자성을 동시에 갖는다 가정= 전자구름

Bohr vs. wave mechanical model

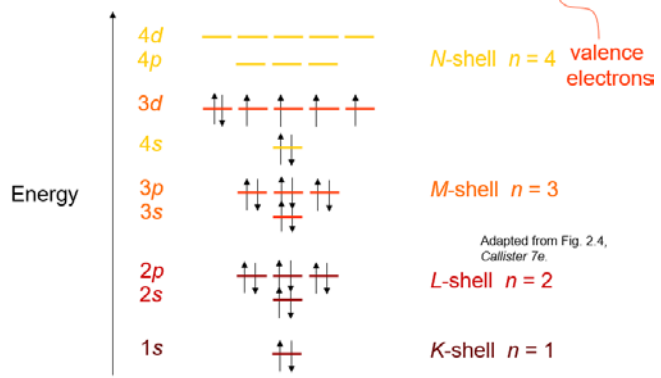


b. Quantum #s (양자수)

n = principal (energy level-shell)	*K*, *L*, *M*, *N*, *O* (1, 2, 3, etc.)
ℓ = subsidiary (orbitals)	*s*, *p*, *d*, *f* (0, 1, 2, 3,…, *n*-1)
m_l = magnetic	1, 3, 5, 7 (-ℓ to +ℓ)
m_s = spin	½, -½

ex: Fe - atomic # = 26 $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^6$ $4s^2$

c. Electron configurations (전자배위)

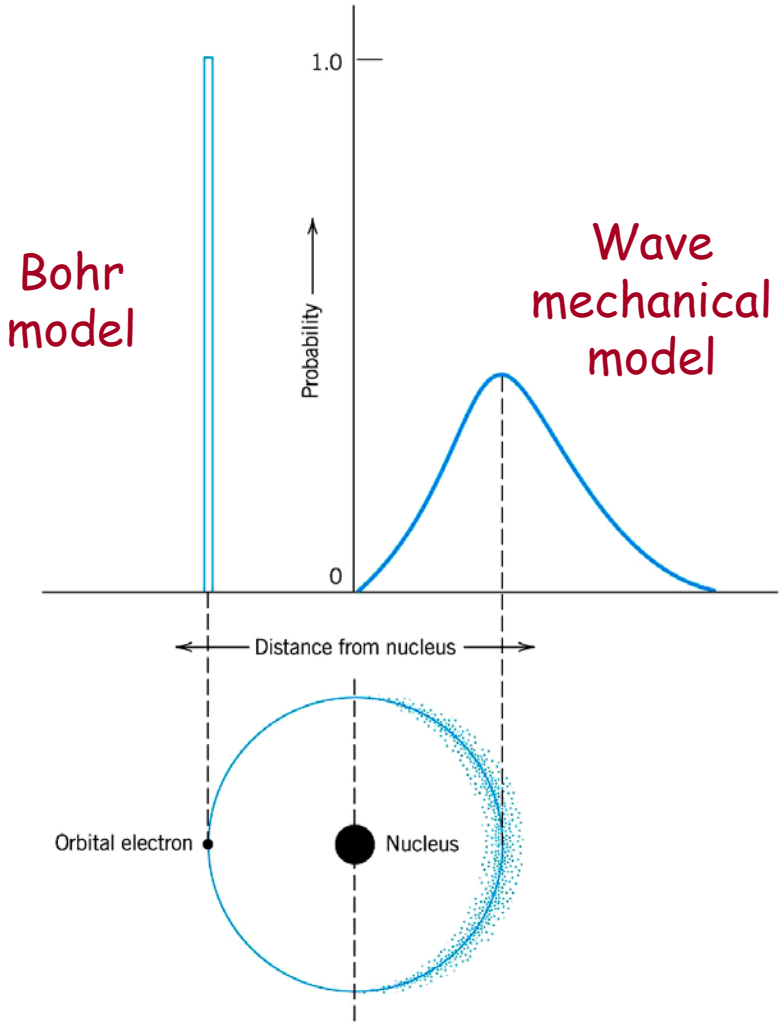


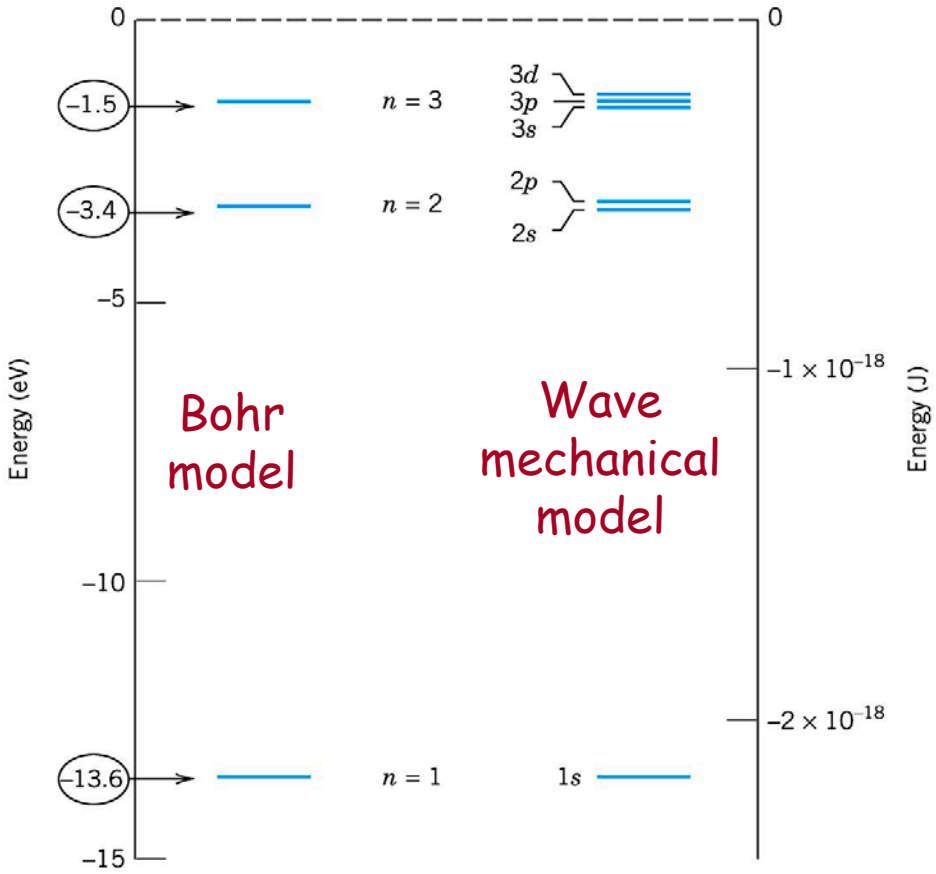
2.4 **Periodic table**

모든 원소는 주기율표 상의 전자 배위에 의해 분류

: 특성의 규칙적인 변화 양상 확인 가능

Bohr vs. wave mechanical model





Electron position is described by a probability distribution or electron cloud

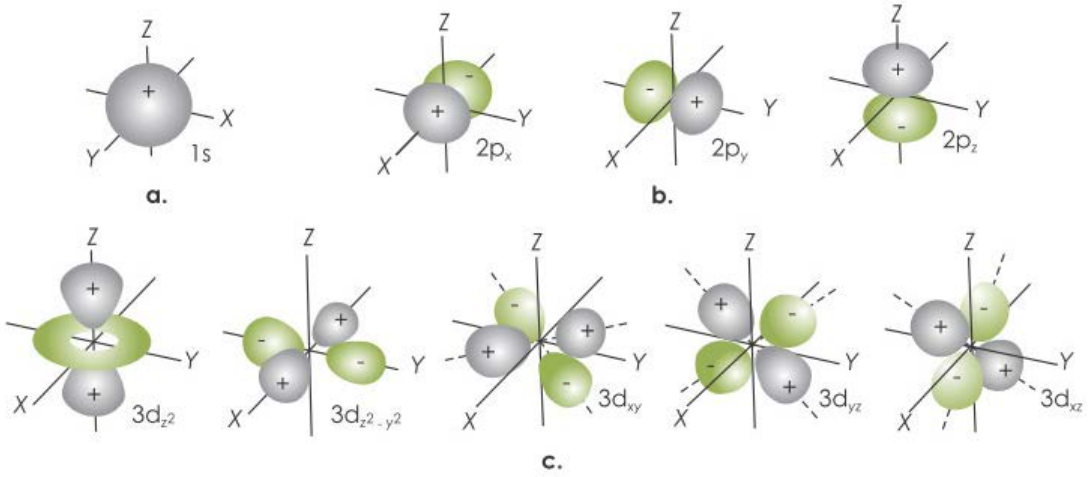
Bohr energy levels to be separated into electron subshells described by quantum numbers

Meaning of quantum numbers

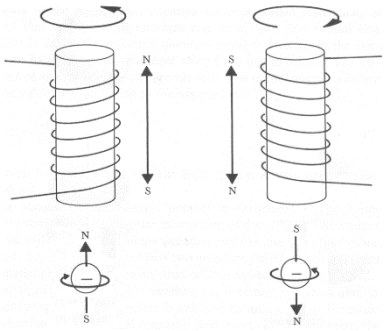
n determines the size

l determines the shape

m_l determines the orientation



Electron spin : $m_s = \pm \frac{\hbar}{2}$



Therefore, complete description of an electron requires **4 quantum numbers**

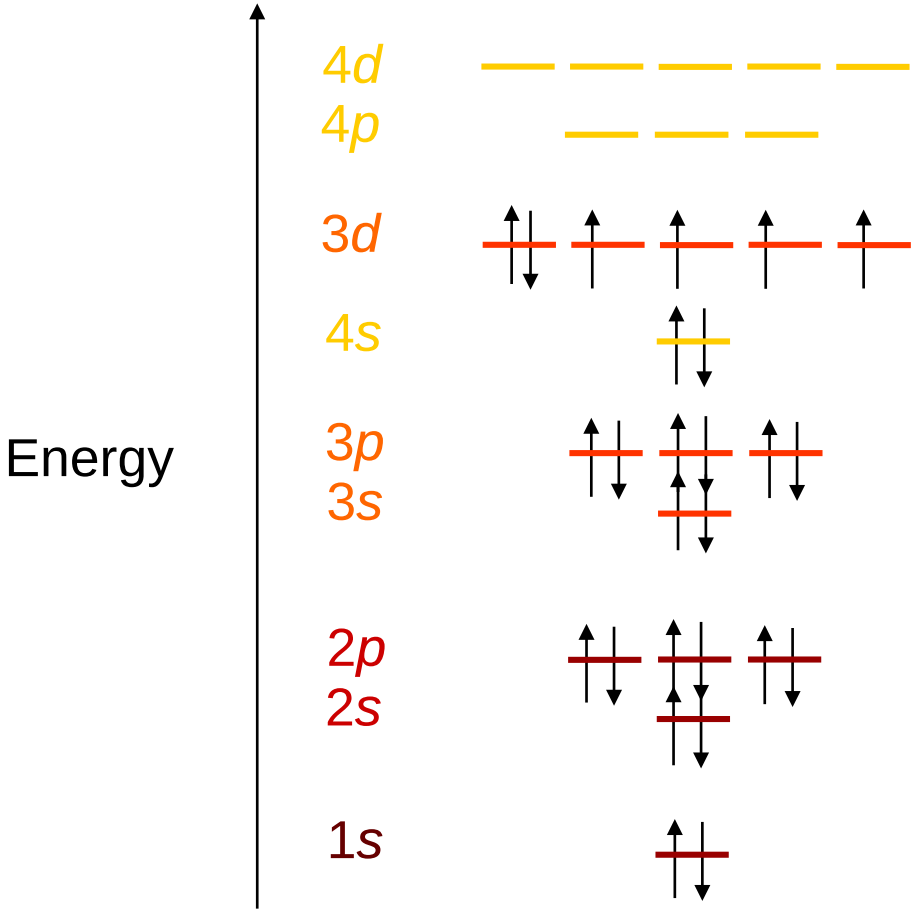
Electronic Configurations

ex: Fe - atomic # = 26 $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^6$ $4s^2$

= 26

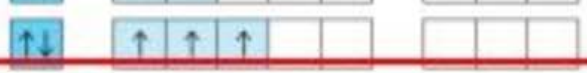
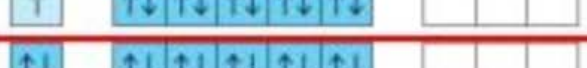
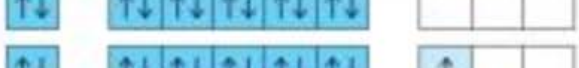
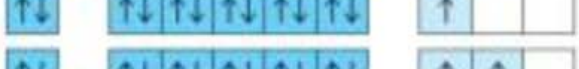
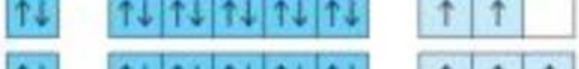
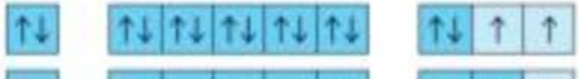
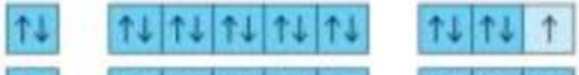
Valence Electrons

(전자들이 에너지가 가장 낮은 상태에 있는 바닥상태에서 반응에 참여할 수 있는 전자)



Adapted from Fig. 2.4, *Callister 7e.*

표 8.3 4주기 원소들의 부분적인 궤도 그림과 전자 배치*

원자번호	원소	부분 궤도 그림(3s, 3p, 3d 부준위만)	총 전자 배치	요약된 전자 배치
		4s 3d 4p		
19	K		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^1$	[Ar] $4s^1$
20	Ca		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2$	[Ar] $4s^2$
21	Sc		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^1$	[Ar] $4s^2 3d^1$
22	Ti		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^2$	[Ar] $4s^2 3d^2$
23	V		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^3$	[Ar] $4s^2 3d^3$
24	Cr		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^1 3d^5$	[Ar] $4s^1 3d^5$
25	Mn		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^5$	[Ar] $4s^2 3d^5$
26	Fe		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^6$	[Ar] $4s^2 3d^6$
27	Co		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^7$	[Ar] $4s^2 3d^7$
28	Ni		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^8$	[Ar] $4s^2 3d^8$
29	Cu		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^1 3d^{10}$	[Ar] $4s^1 3d^{10}$
30	Zn		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^{10}$	[Ar] $4s^2 3d^{10}$
31	Ga		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^{10} 4p^1$	[Ar] $4s^2 3d^{10} 4p^1$
32	Ge		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^{10} 4p^2$	[Ar] $4s^2 3d^{10} 4p^2$
33	As		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^{10} 4p^3$	[Ar] $4s^2 3d^{10} 4p^3$
34	Se		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^{10} 4p^4$	[Ar] $4s^2 3d^{10} 4p^4$
35	Br		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^{10} 4p^5$	[Ar] $4s^2 3d^{10} 4p^5$
36	Kr		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^{10} 4p^6$	[Ar] $4s^2 3d^{10} 4p^6$

* 색으로 표시된 것은 마지막 전자가 더해진 부준위를 표시한다.

SURVEY OF ELEMENTS

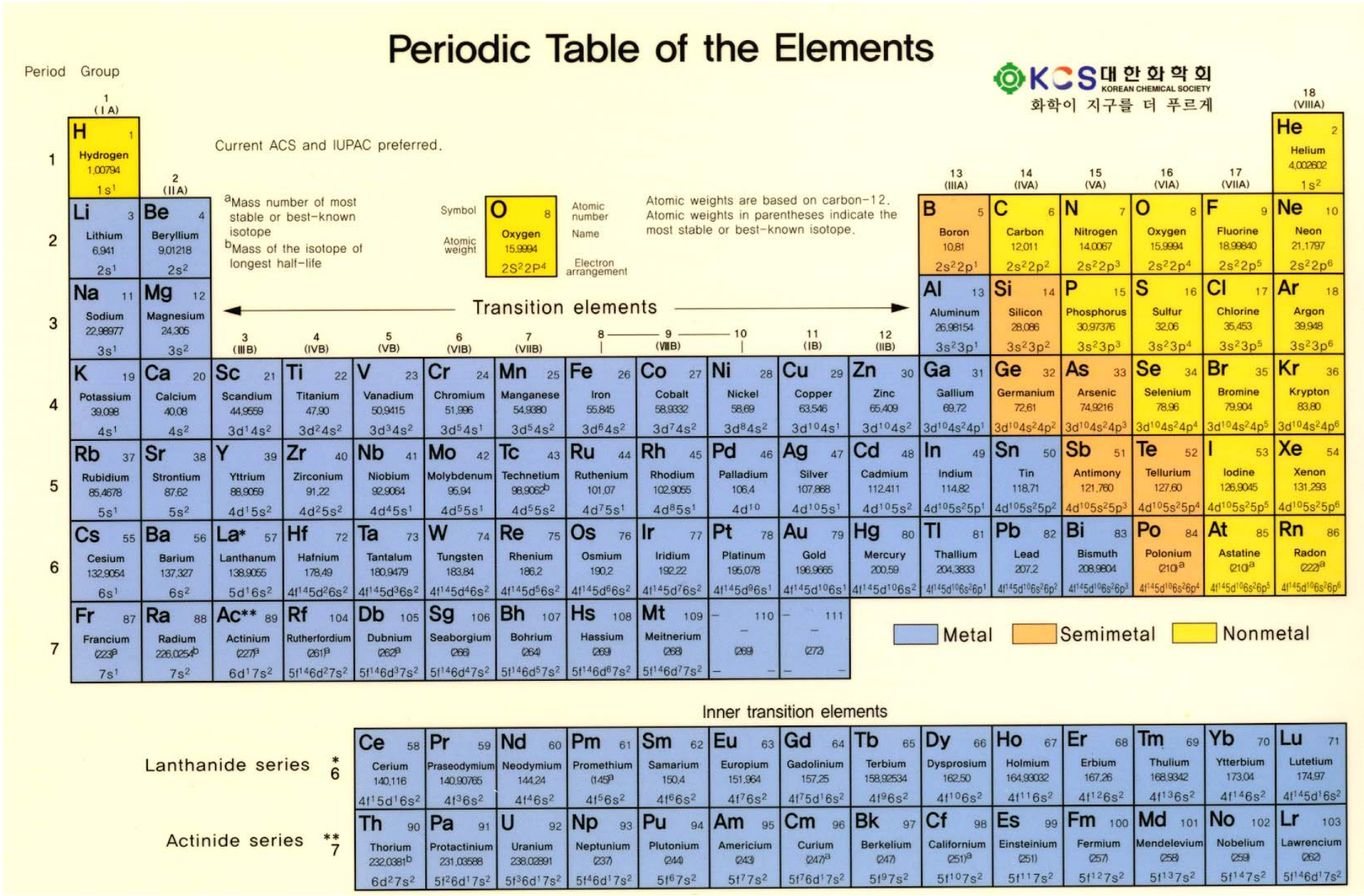
- Most elements: Electron configuration not stable.

Element	Atomic #	Electron configuration	
Hydrogen	1	$1s^1$	
Helium	2	$1s^2$	(stable)
Lithium	3	$1s^2 2s^1$	
Beryllium	4	$1s^2 2s^2$	
Boron	5	$1s^2 2s^2 2p^1$	
Carbon	6	$1s^2 2s^2 2p^2$	
...		...	
Neon	10	$1s^2 2s^2 2p^6$	(stable)
Sodium	11	$1s^2 2s^2 2p^6 3s^1$	
Magnesium	12	$1s^2 2s^2 2p^6 3s^2$	
Aluminum	13	$1s^2 2s^2 2p^6 3s^2 3p^1$	
...		...	
Argon	18	$1s^2 2s^2 2p^6 3s^2 3p^6$	(stable)
...	...	...	
Krypton	36	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$	(stable)

Adapted from Table 2.2, *Callister 7e.*

- Why? Valence (outer) shell usually not filled completely.

Chapter 2.4 모든 원소는 주기율표 상의 전자 배위에 의해 분류



CHAPTER 2:
Atomic structure and Interatomic bonding

; 많은 경우 결합의 종류로 재료의 특성 설명

ISSUES TO ADDRESS...

- What promotes bonding?
- What types of bonds are there?
- What properties are inferred from bonding?

Contents for today's class

Atomic Bonding in Solids

- Primary interatomic bonds

a. Ionic / b. covalent / c. metallic

- Secondary bonds

a. Van der Waals / b. Hydrogen

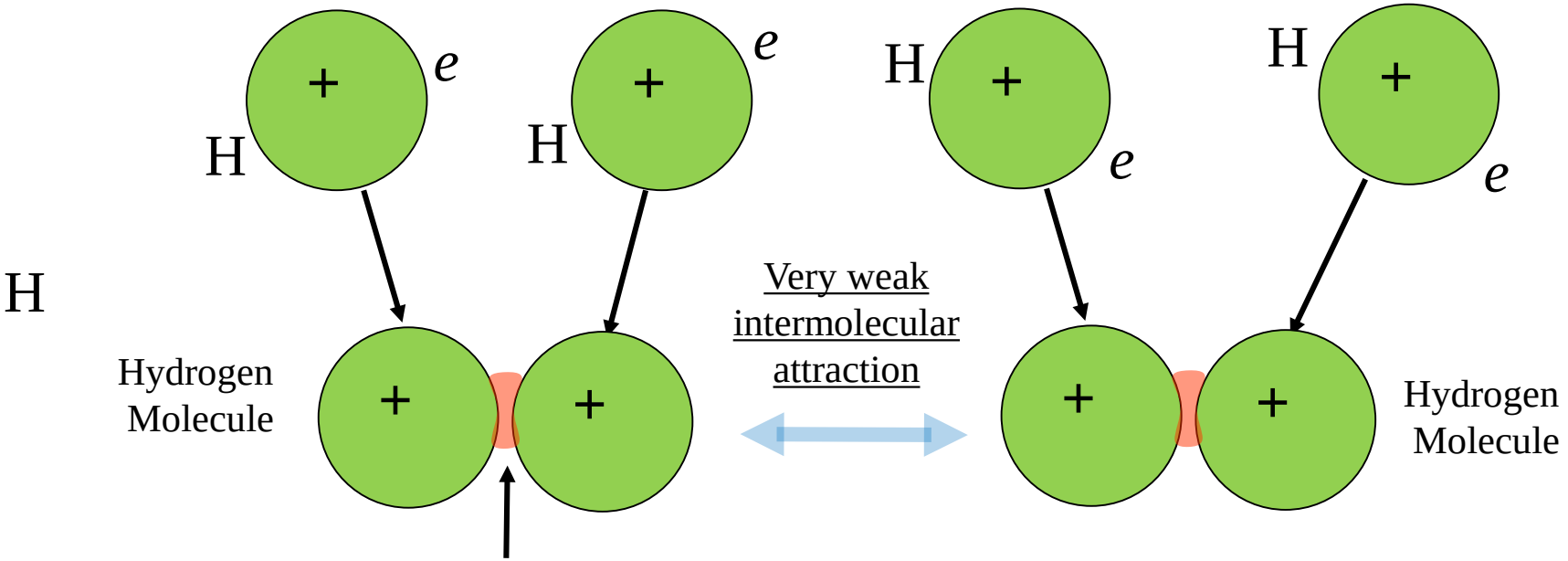
- Properties from bonding

Fundamental Concepts

❑ Two fundamental types of bonding:

❑ **primary bonds**: strong atom-to-atom attractions produced by changes in electron position of the ***valence e***$^-$. *Example : covalent atom between two hydrogen atoms*

❑ **secondary bonds**: much weaker. It is the attraction due to overall "electric fields", often resulting from electron transfer in primary bonds. *Example: intramolecular bond between H_2 molecules*



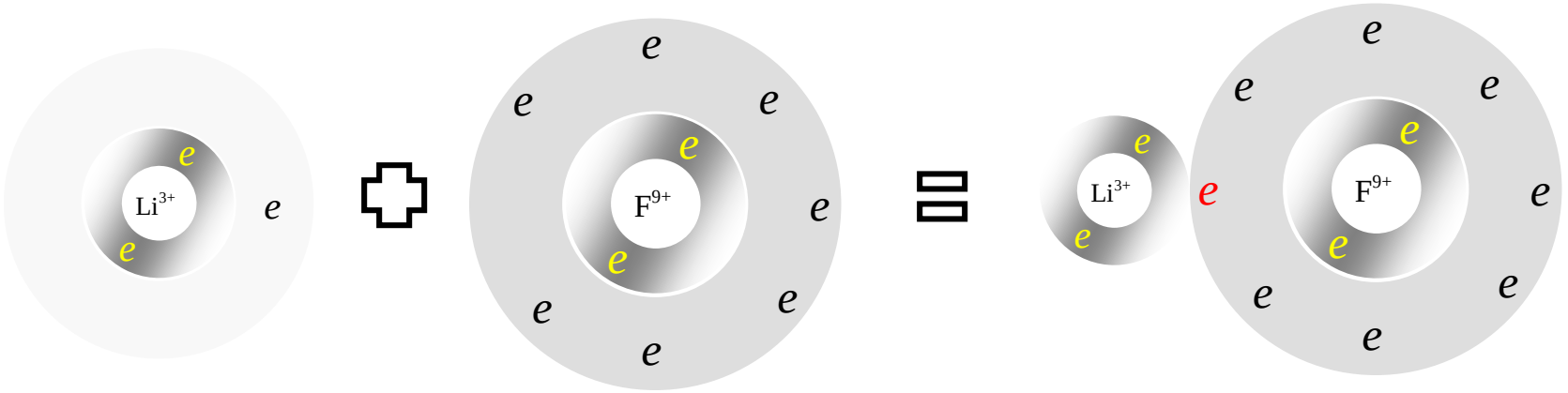
Chapter 2.6 Primary interatomic bonds (or Chemical bonds)

각 결합은 최외각 전자에 의함/ 결합 방식은 구성원자의 전자구조에 의함

a. IONIC

Atomic bonding

When atoms of far- & near-closed shell structure are brought together …



Atoms of far-closed shell structure & near-closed one tend to lose & gain electrons, respectively

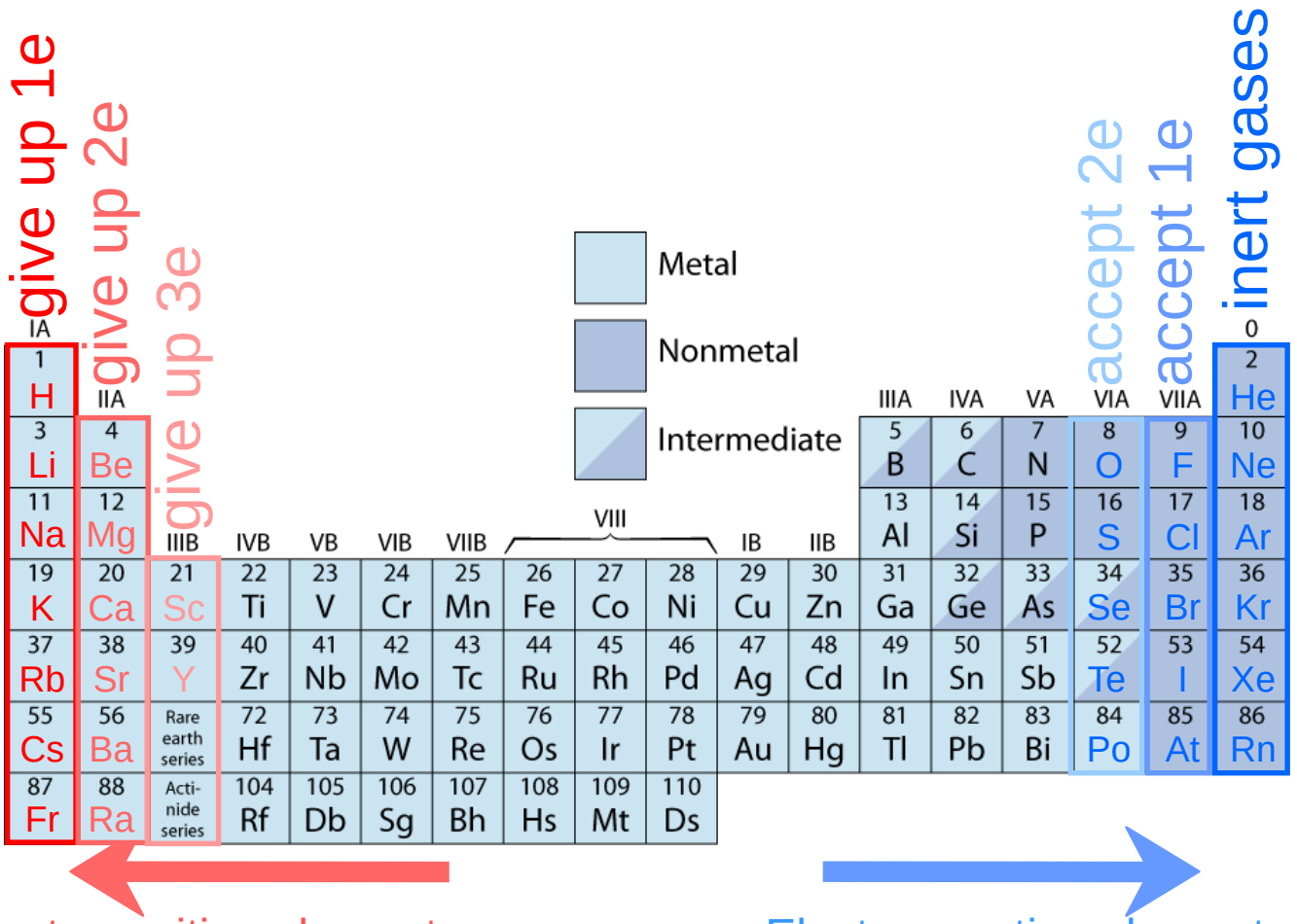
→ Electronegativity by L. Pauling

Excess charge induced by the transfer of electrons are compensated by the presence of ions of opposite sign

➔ Ionic bonding

The Periodic Table

- Columns: Similar Valence Structure



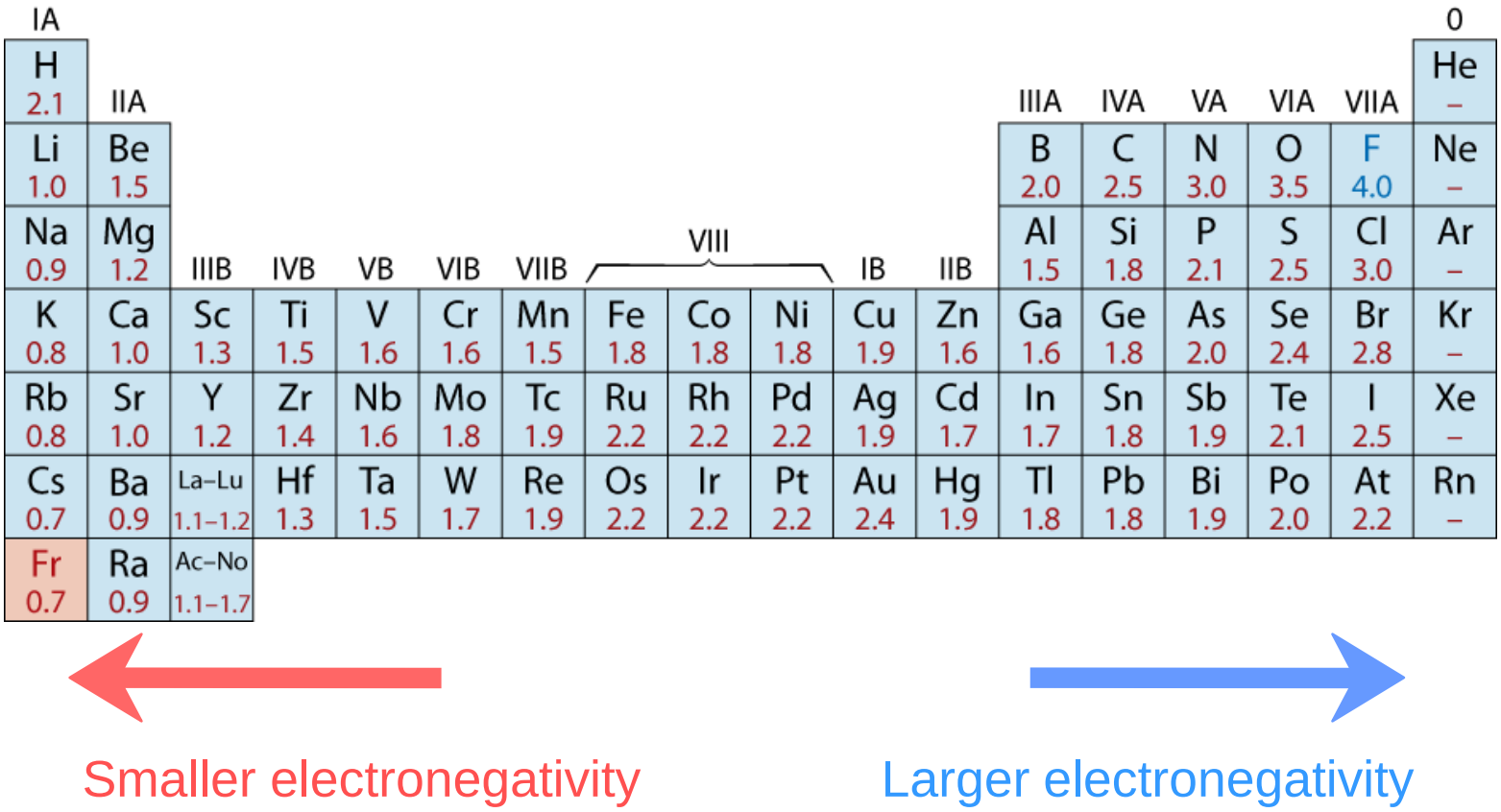
Adapted from Fig. 2.6, *Callister 7e.*

Electropositive elements: Readily give up electrons to become + ions.

Electronegative elements: Readily acquire electrons to become - ions.

Electronegativity

- Ranges from 0.7 to 4.0,
- Large values: tendency to acquire electrons.



Adapted from Fig. 2.7, *Callister 7e.* (Fig. 2.7 is adapted from Linus Pauling, *The Nature of the Chemical Bond*, 3rd edition, Copyright 1939 and 1940, 3rd edition. Copyright 1960 by Cornell University.

Ionic bond = metal + nonmetal

Donates electrons

Accepts electrons

Dissimilar electronegativities

ex: MgO

Mg $1s^2\ 2s^2\ 2p^6\ 3s^2$ = [Ne] $3s^2$

O $1s^2\ 2s^2\ 2p^4$

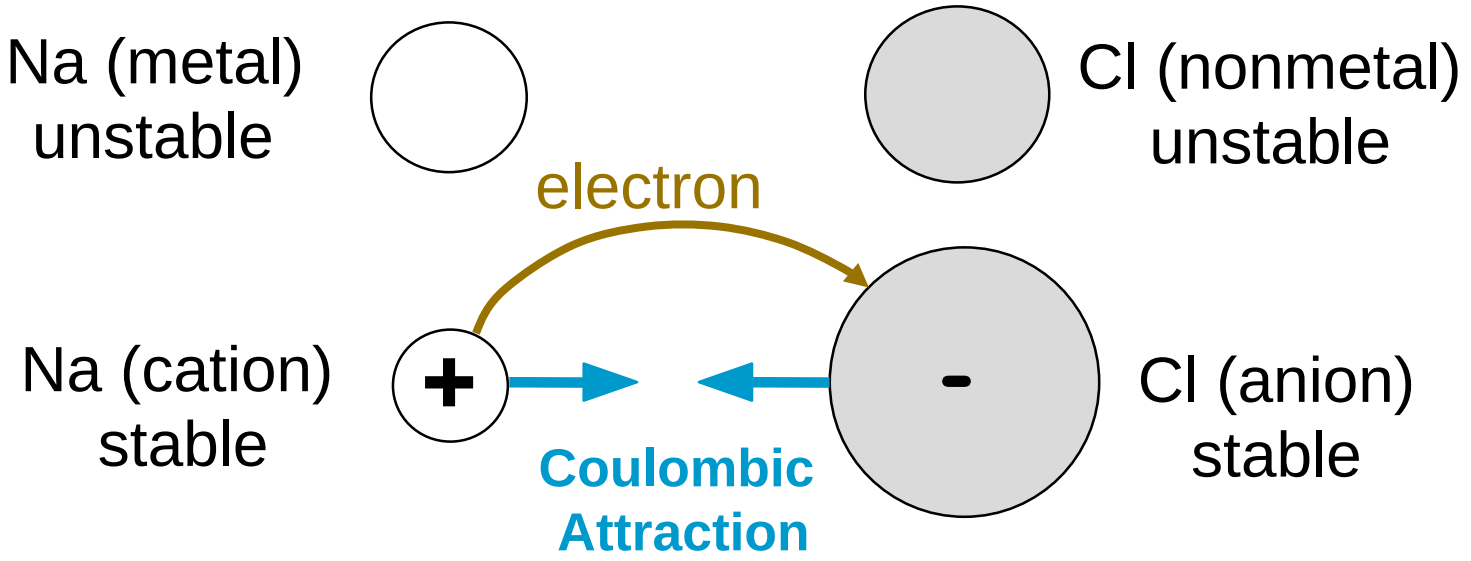
Mg^{2+} $1s^2\ 2s^2\ 2p^6$ = [Ne]

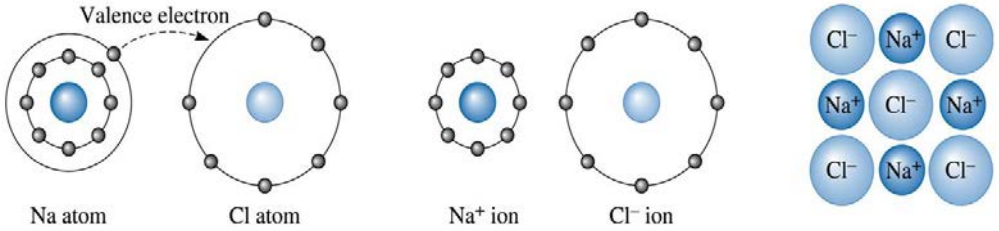
O^{2-} $1s^2\ 2s^2\ 2p^6$ = [Ne]

Ionic Bonding

- Occurs between + and – ions
- Requires electron transfer
- Large difference in electronegativity required

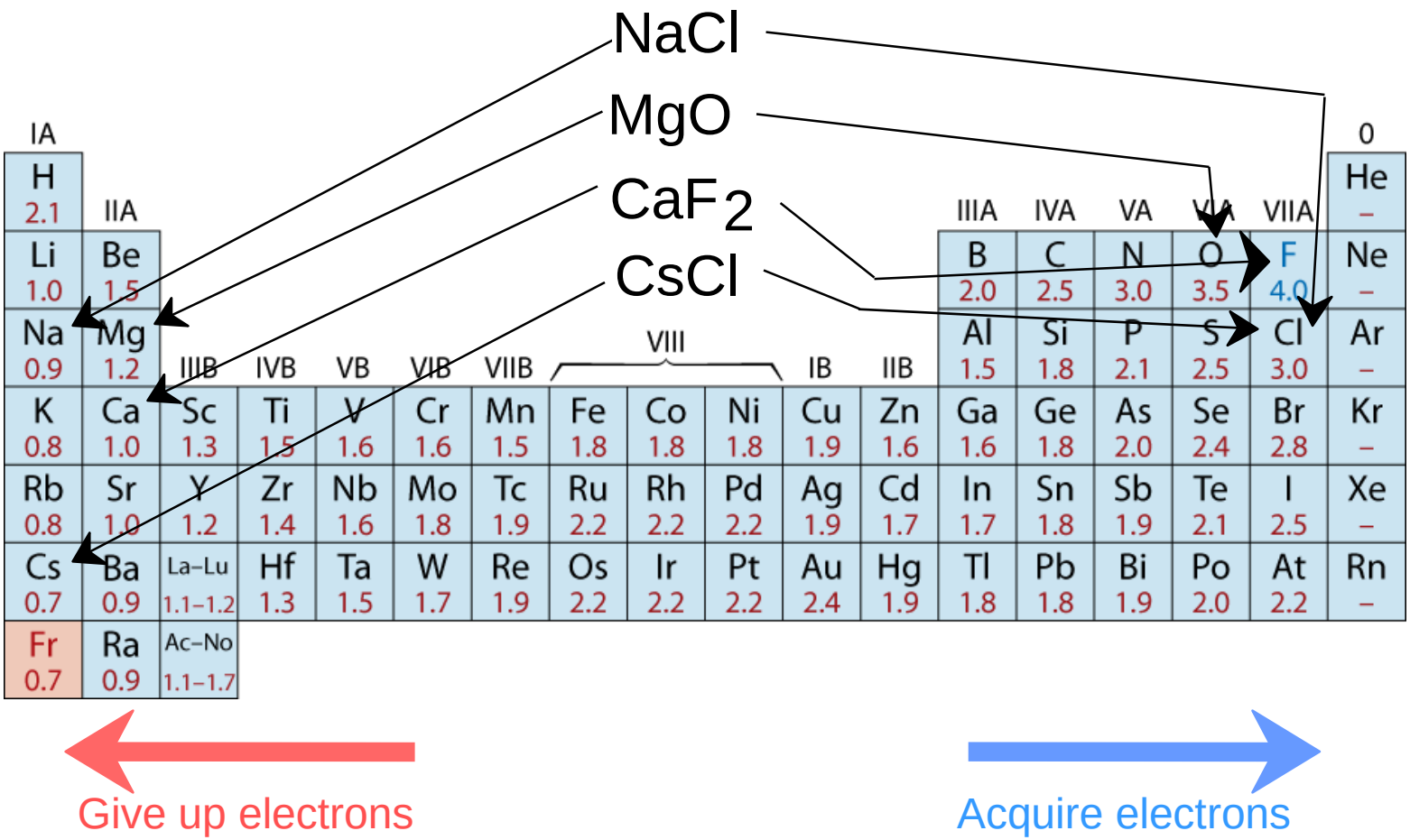
- Example: NaCl



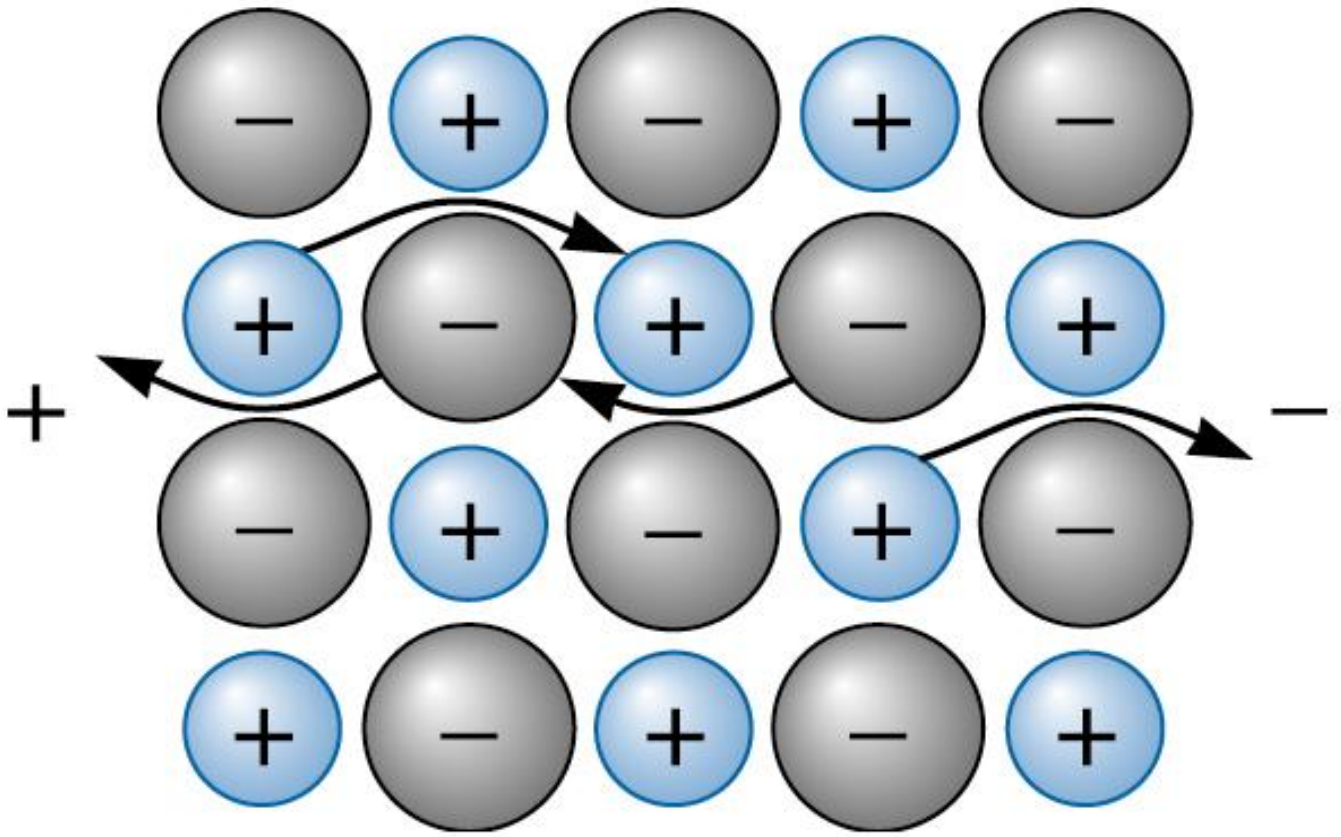


Examples: Ionic Bonding

- Predominant bonding in Ceramics



Adapted from Fig. 2.7, *Callister 7e.* (Fig. 2.7 is adapted from Linus Pauling, *The Nature of the Chemical Bond*, 3rd edition, Copyright 1939 and 1940, 3rd edition. Copyright 1960 by Cornell University.



- When voltage is applied to an ionic material, entire ions must move to cause a current to flow. → Ion movement is slow and the electrical conductivity is poor.

Ionic Crystal

Table 7 Properties of alkali halide crystals with the NaCl structure

All values (except those in brackets) at room temperature and atmospheric pressure, with no correction for changes in R_0 and U from absolute zero. Values in brackets at absolute zero temperature and zero pressure, from private communication by L. Brewer.

	Nearest-neighbor separation R_0, in Å	Bulk modulus B, in 10^{11} dyn/cm^2 or 10^{10} N/m^2	Repulsive energy parameter $z\lambda$, in 10^{-8} erg	Repulsive range parameter ρ, in Å	Lattice energy compared to free ions, in kcal/mol	
					Experimental	Calculated
LiF	2.014	6.71	0.296	0.291	242.3[246.8]	242.2
LiCl	2.570	2.98	0.490	0.330	198.9[201.8]	192.9
LiBr	2.751	2.38	0.591	0.340	189.8	181.0
LiI	3.000	(1.71)	0.599	0.366	177.7	166.1
NaF	2.317	4.65	0.641	0.290	214.4[217.9]	215.2
NaCl	2.820	2.40	1.05	0.321	182.6[185.3]	178.6
NaBr	2.989	1.99	1.33	0.328	173.6[174.3]	169.2
NaI	3.237	1.51	1.58	0.345	163.2[162.3]	156.6
KF	2.674	3.05	1.31	0.298	189.8[194.5]	189.1
KCl	3.147	1.74	2.05	0.326	165.8[169.5]	161.6
KBr	3.298	1.48	2.30	0.336	158.5[159.3]	154.5
KI	3.533	1.17	2.85	0.348	149.9[151.1]	144.5
RbF	2.815	2.62	1.78	0.301	181.4	180.4
RbCl	3.291	1.56	3.19	0.323	159.3	155.4
RbBr	3.445	1.30	3.03	0.338	152.6	148.3
RbI	3.671	1.06	3.99	0.348	144.9	139.6

Data from various tables by M. P. Tosi, Solid state physics **16**, 1 (1964).

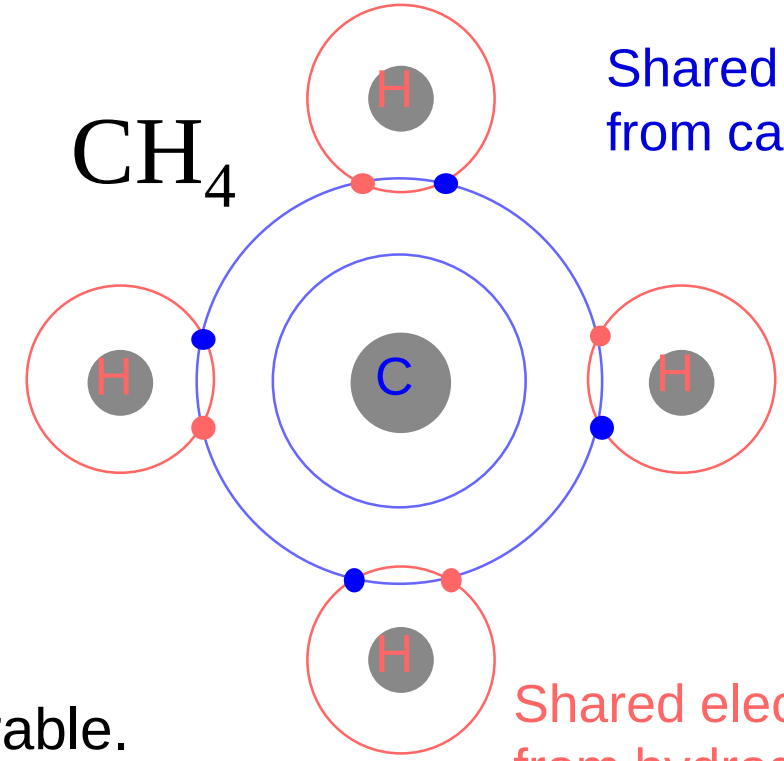
b. COVALENT

Covalent Bonding

- similar electronegativity ∴ share electrons
- bonds determined by valence – *s* & *p* orbitals dominate bonding
- Example: CH_4

C: has 4 valence e^-, needs 4 more

H: has 1 valence e^-, needs 1 more



Electronegativities are comparable.

Covalent Bonding: Bond Hybrization 혼성화

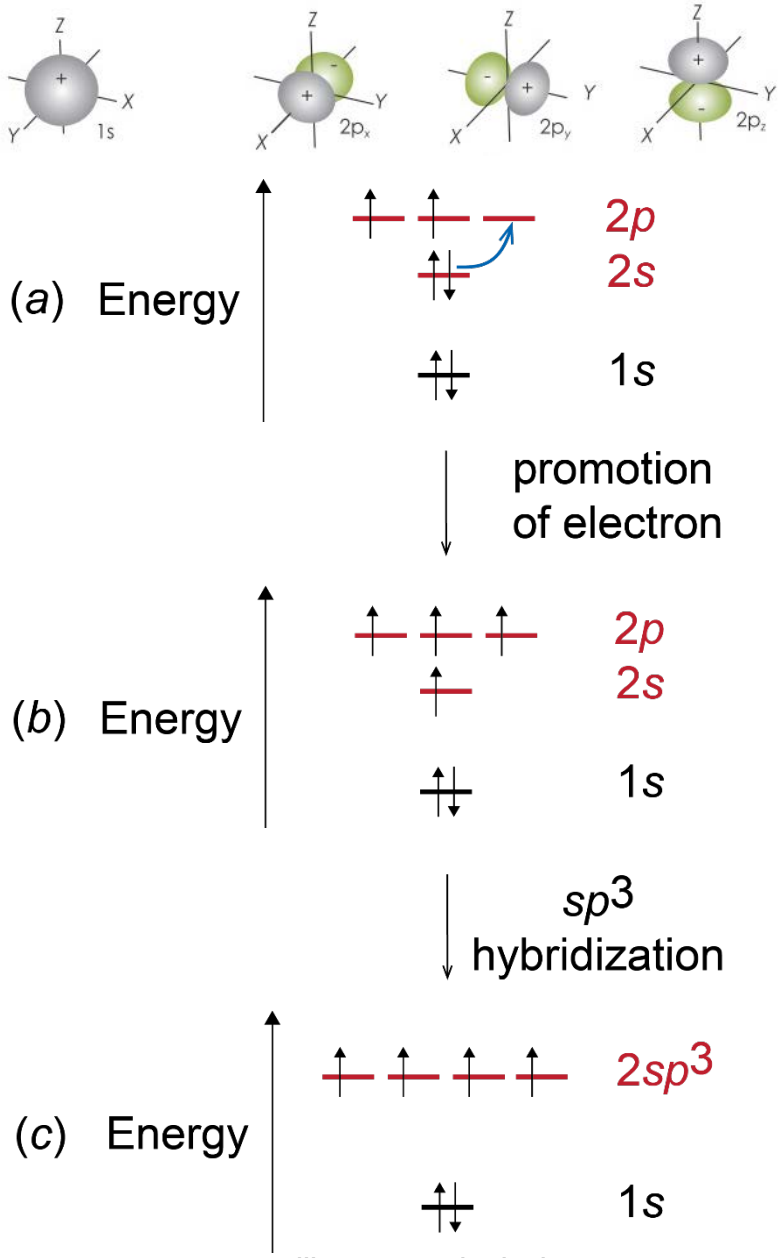


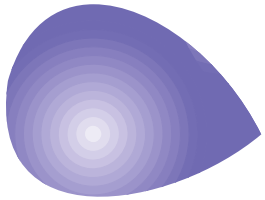
Fig. 2.13, *Callister & Rethwisch 10e.*

2개 이상의 원자궤도가 결합시 궤도의 공유를 최대한으로 하기 위해 합쳐지는 현상

* Carbon can form sp^3 hybrid orbitals

Carbon $1s^2 2s^2 2p^2 \rightarrow 1s^2 2s^1 2p^3$:

2s와 2p 궤도가 합쳐져 4개의 sp^3 가 됨



sp^3 궤도는 동일방향의 스핀을 갖고 다른 원자와 공유결합이 가능한 형태임.

Fig. 2.14, *Callister & Rethwisch 10e.*
(Adapted from J.E. Brady and F. Senese, *Chemistry: Matter and Its Changes*, 4th edition. Reprinted with permission of John Wiley and Sons, Inc.)

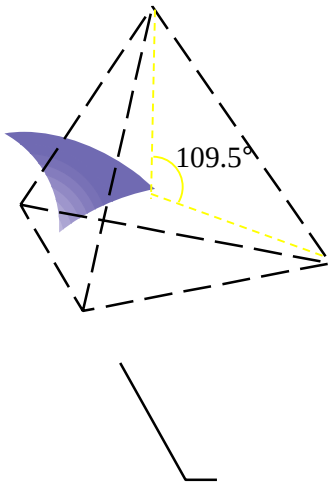
Covalent Bonding (cont.)

Hybrid sp^3 bonding involving carbon

Example: CH_4

C: each has 4 valence electrons, needs 4 more

H: each has 1 valence electron, needs 1 more



Electronegativities of C and H are similar so electrons are shared in sp^3 hybrid covalent bonds.

혼성화 궤도는 방향성을 갖음 = 인접 결합 원자와 궤도 공유

Fig. 2.15, *Callister & Rethwisch 10e.*
(Adapted from J.E. Brady and F. Senese, *Chemistry: Matter and Its Changes*, 4th edition. Reprinted with permission of John Wiley and Sons, Inc.)

* 탄소나 일부 재료에서 다른 혼성 결합도 나타남

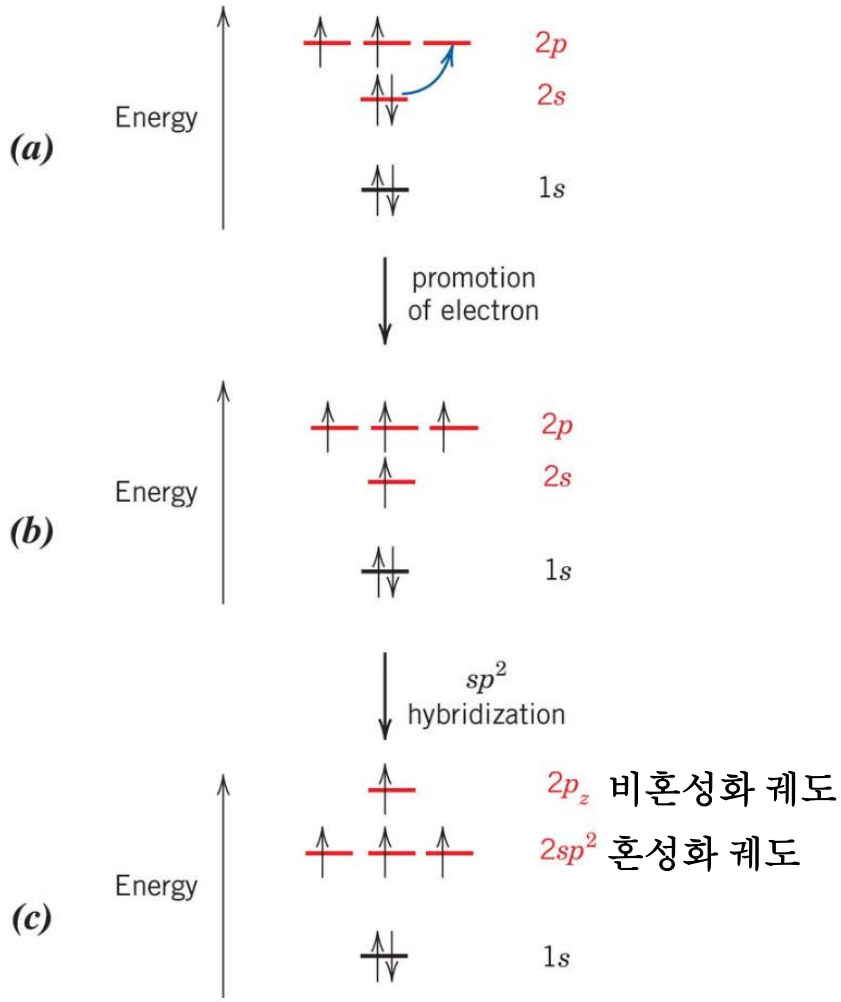


Fig. 2.16 탄소에서 sp^2 혼성 궤도의 형성. (a) 2*s* 전자가 *sp* 준위로 전이, (b) 2*p* 준위의 전자 배치, (c) 1개의 2*s* 궤도와 2개의 2*p* 궤도가 혼성되어 3개의 $2sp^2$를 형성

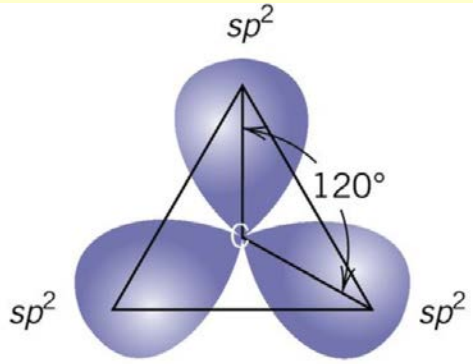


Fig. 2.17 동일 평면상에 있고 삼각형의 꼭지점을 향하는 3개의 sp^2 궤도. 인접궤도간의 각도는 120°

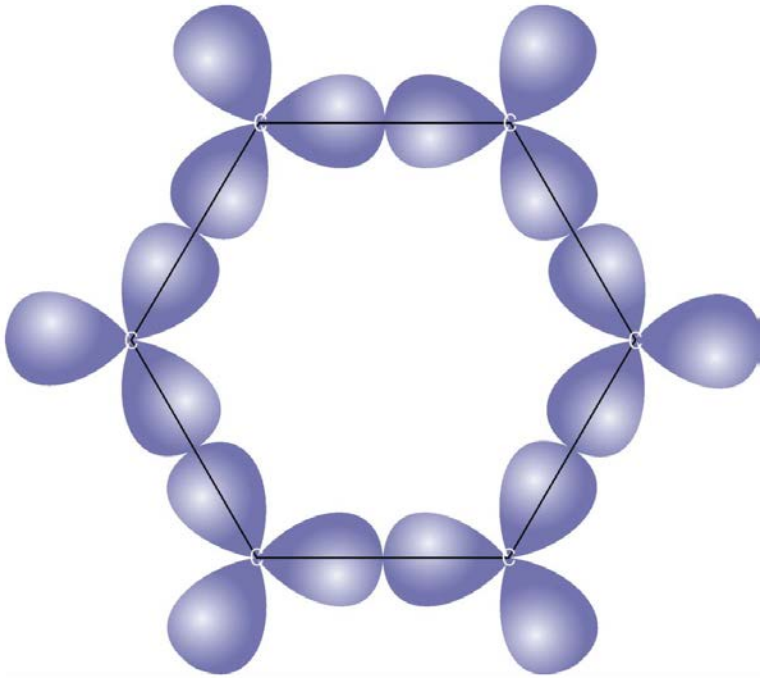
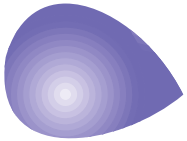


Fig. 2.18 6개의 sp^2 삼각형 간의 결합에 의한 육각형의 형성



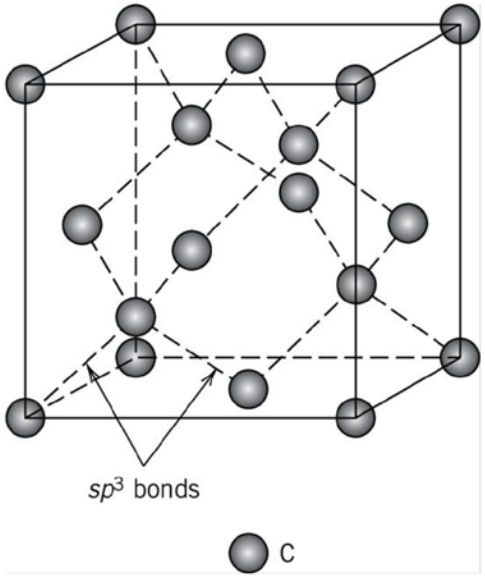
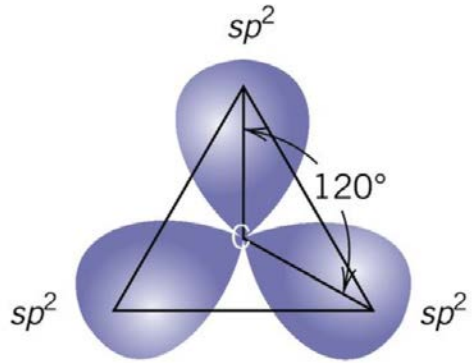


Fig. 12.16 다이아몬드 입방 결정구조



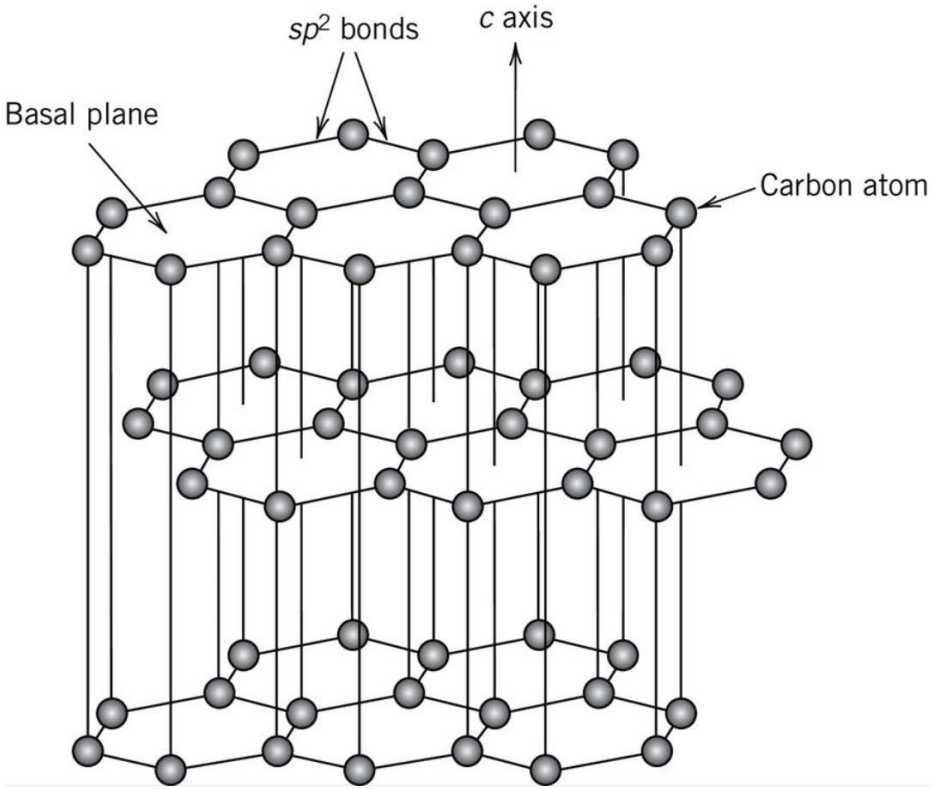
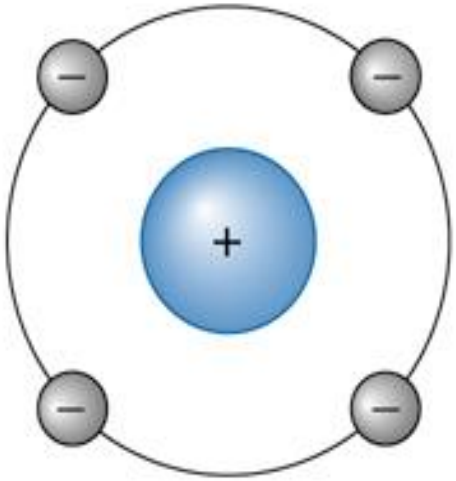
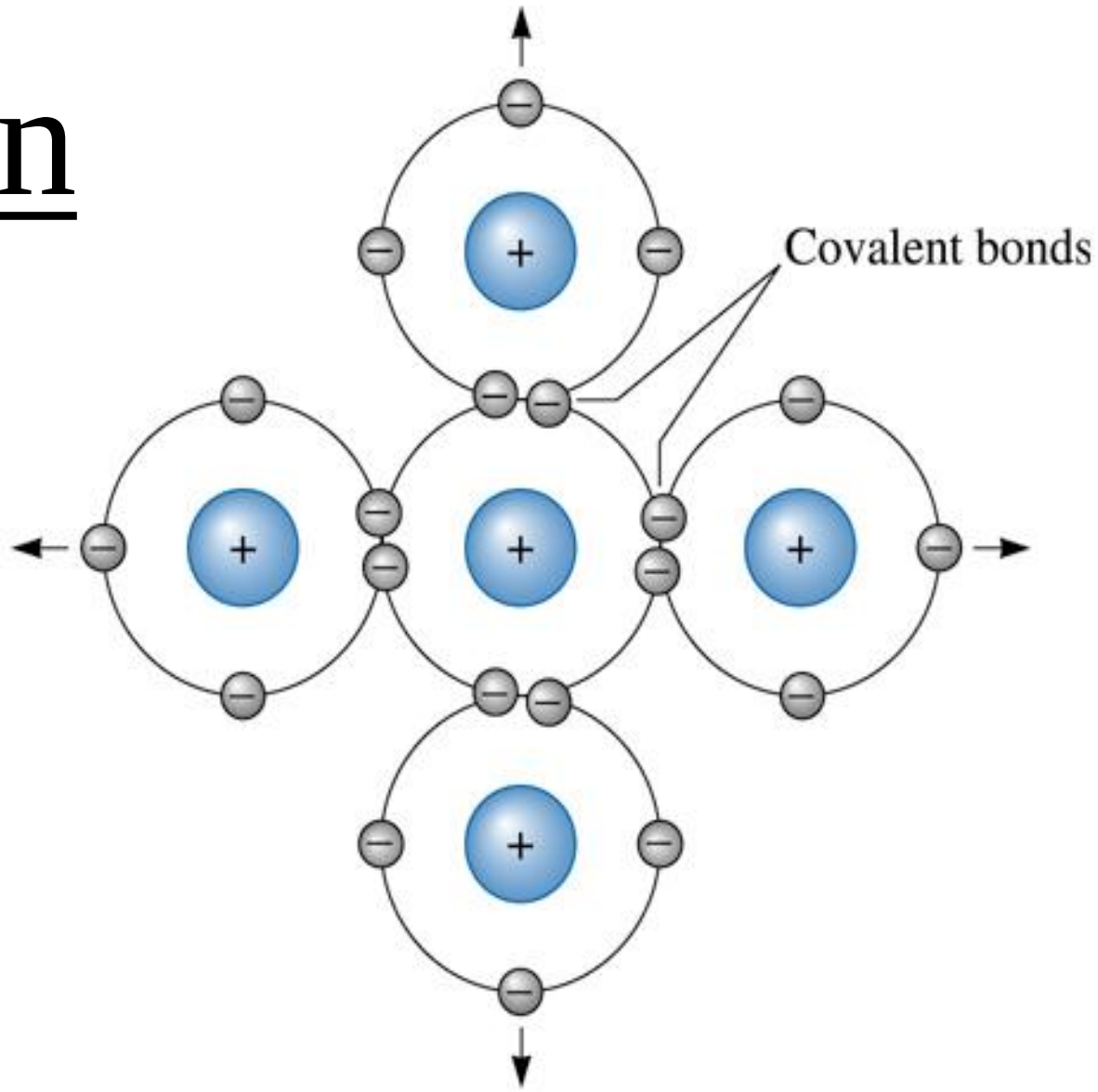


Fig. 12.17 흑연의 구조

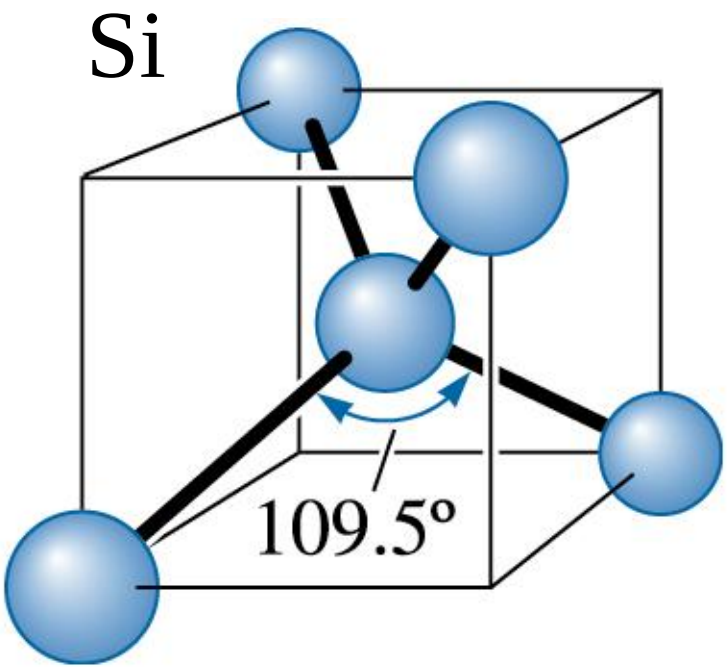
Silicon



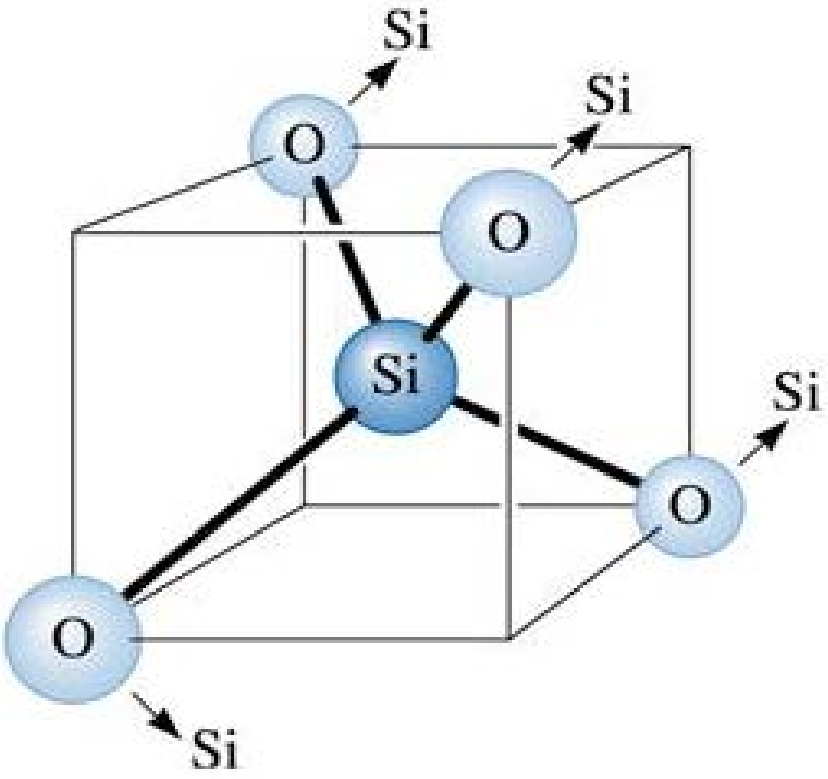
Silicon atom



Covalent Bonding



VS.



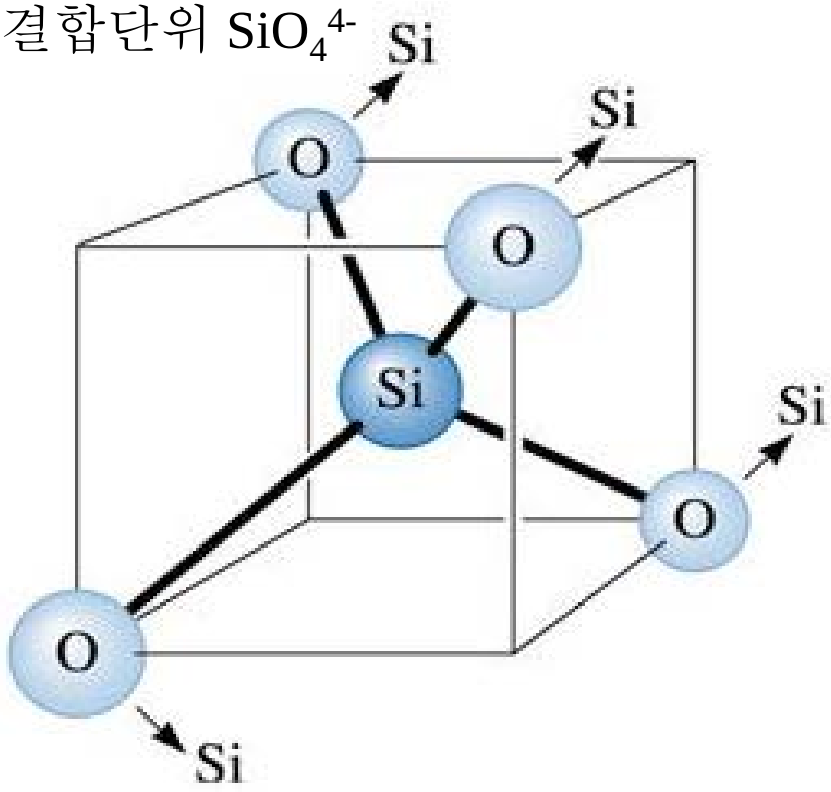
- The tetrahedral structure of silica ($Si0_2$), which contains covalent bonds between silicon and oxygen atoms

Covalent Bonding

Most common elements on earth are Si & O

short-ranged arrangement

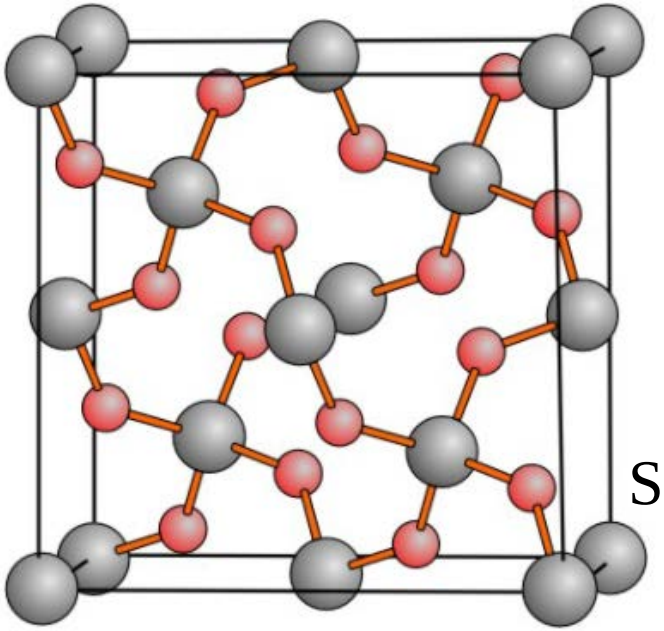
결합단위 SiO_4^{4-}



VS.

long-ranged arrangement

Unit cell



Si_8O_{16}

Figure 8.26: Structure of High Cristobalite, a Form of Quartz

- The tetrahedral structure of silica (SiO_2), which contains covalent bonds between silicon and oxygen atoms

Silicates

Bonding of adjacent SiO_4^{4-} accomplished by the **sharing of common corners, edges, or faces**

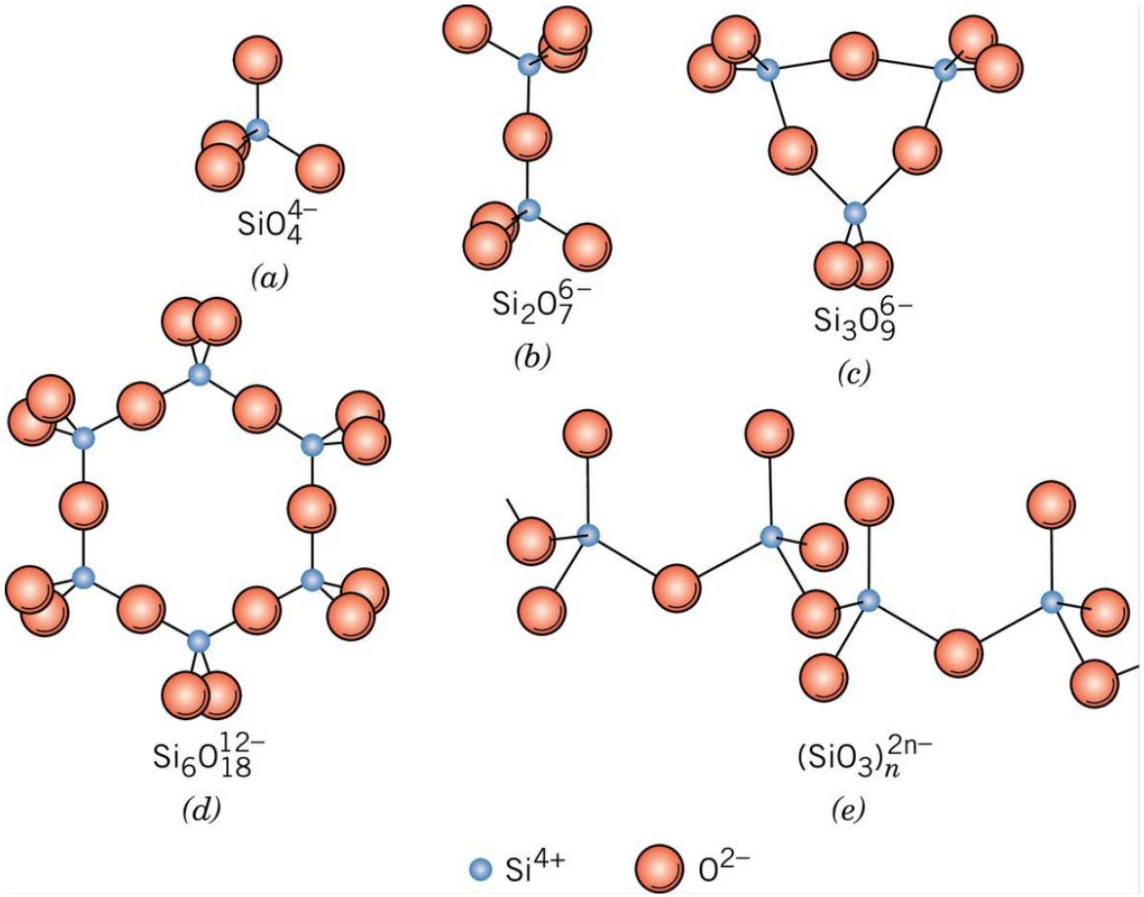
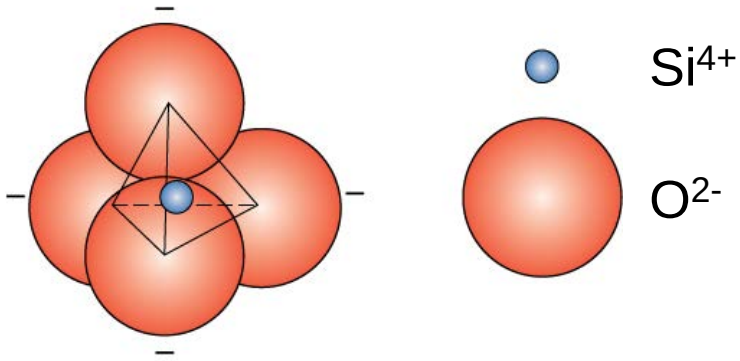
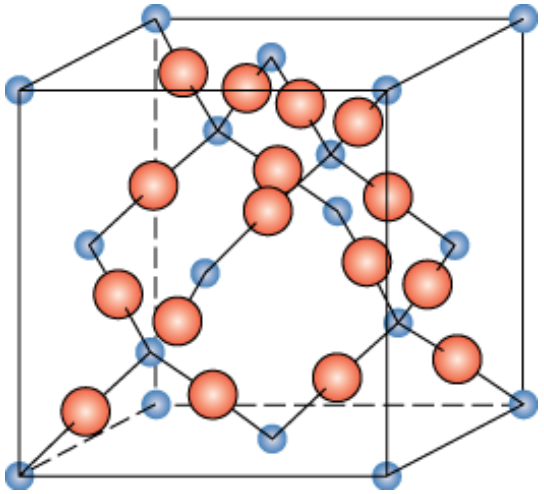


Fig. 12.12 Five silicate ion structures formed from SiO_4^{4-} tetrahedra

- Most crystals are composed of a limited and simple number of components, E.g. SiO_2, Mg_2SiO_4. This is because **a crystal is composed of a small number of atoms in a minimum energy arrangement that displays translational periodicity.** As a consequence, and making use of the **concept of coordinated polyhedra**, **there are a limited number of ways to pack the atoms together to form a solid.**
- Presently, **about 50 different phases of SiO_2 (silica)** have been discovered, such as quartz, crystobalite, & tridymite …



Figs. 4.10 & 4.11, *Callister & Rethwisch 9e*



Crystobalite, a polymorph of SiO_2

Mg_2SiO_4 $Ca_2MgSi_2O_7$

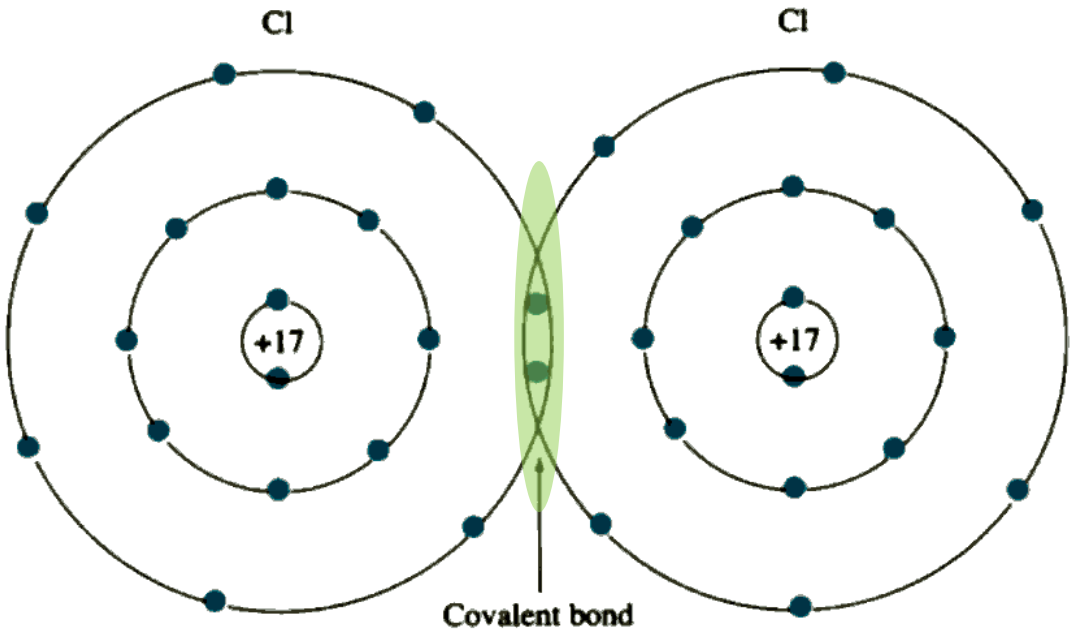
Presence of cations such as Ca^{2+}, Mg^{2+}, & Al^{3+}

1. maintain charge neutrality, and
2. ionically bond SiO_4^{4-} to one another

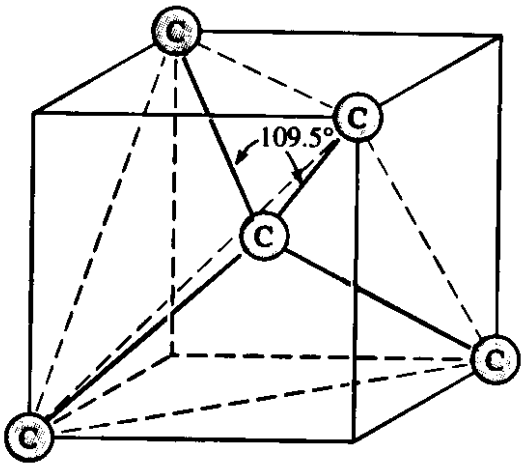
Covalent Bonding : Electron sharing, directional

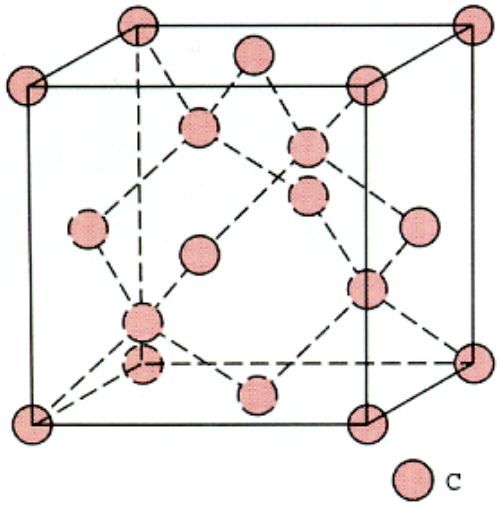
= 인접 결합 원자와 궤도 공유

Cl_2

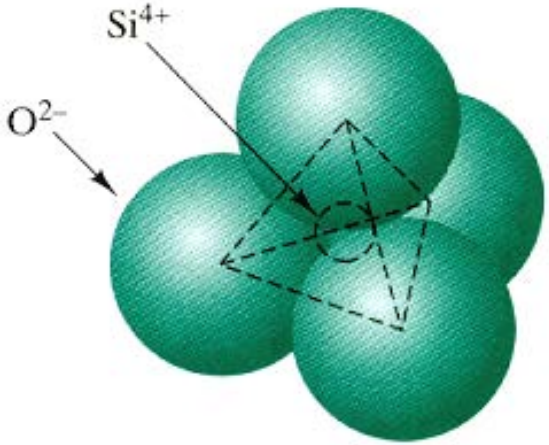


diamond

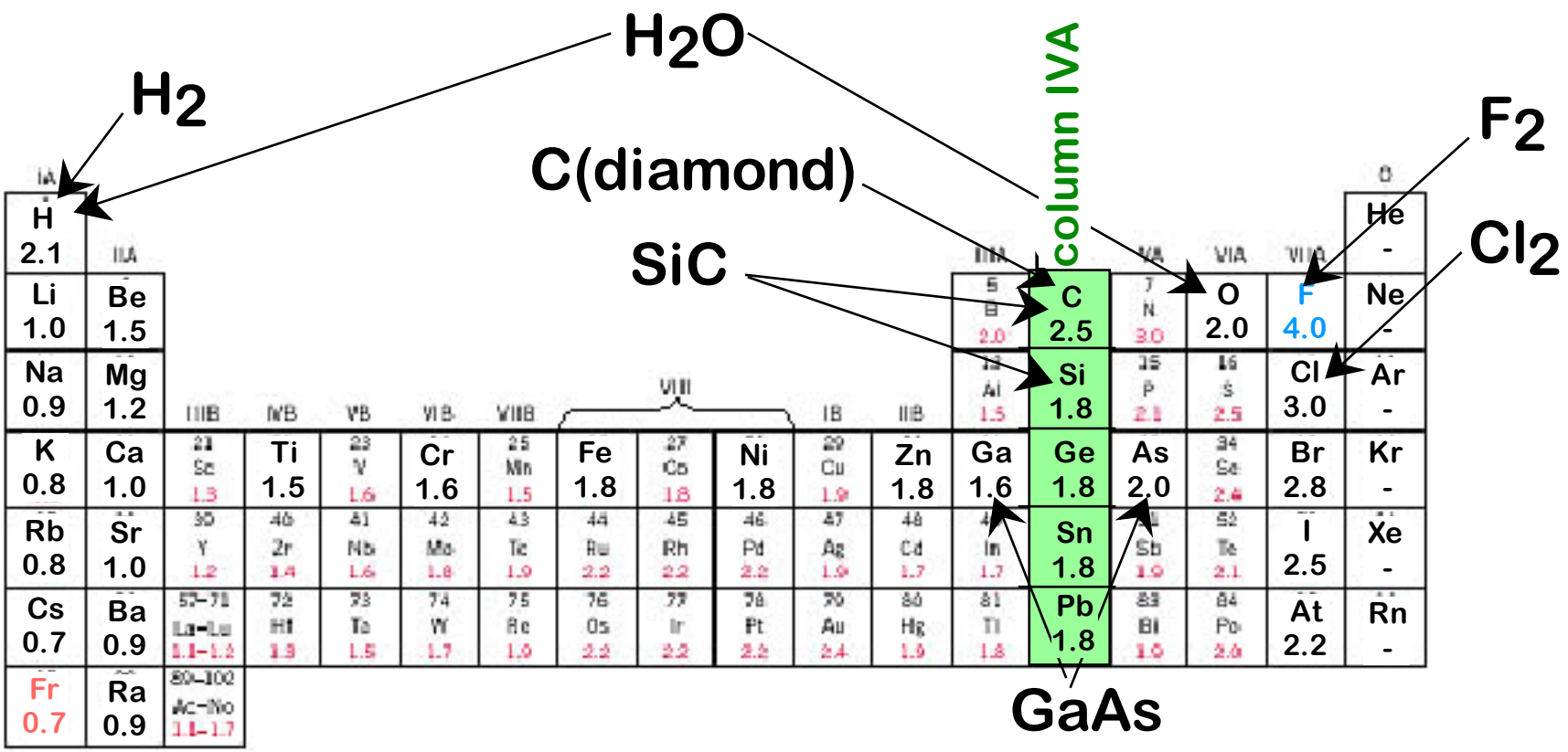




SiO_4^{2-}



Example : Covalent Bonding



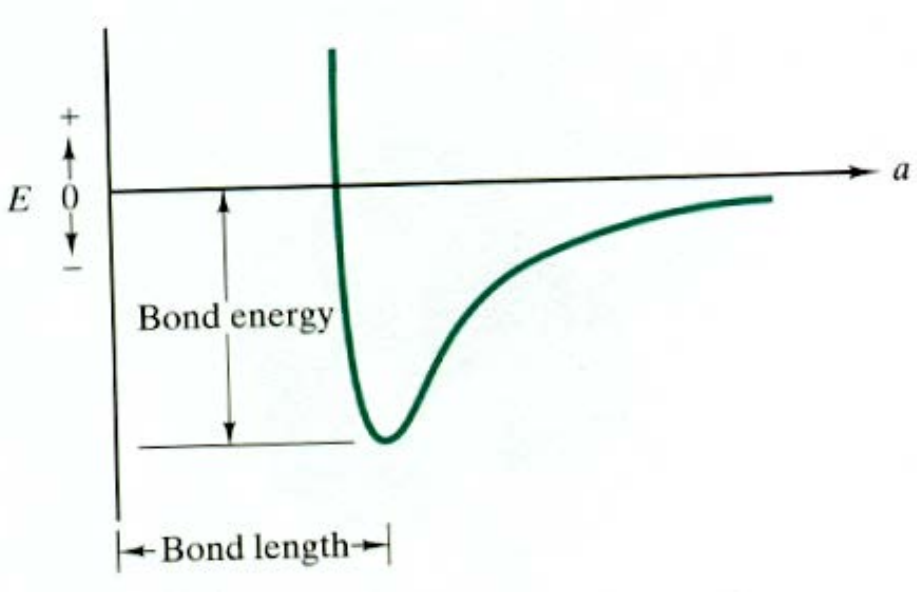
left-hand side metals

- molecules with nonmetals
- molecules with metals and nonmetals
- elemental solids (RHS of Periodic Table)
- compound solids (about column IVA)

right-hand side non-metals

Covalent Bonding

- Bond energy curve



- Strong directional nature of bonding
- Wide range of hardness & melting point

  ex. High (Diamond) or low (Bismuth) melting point

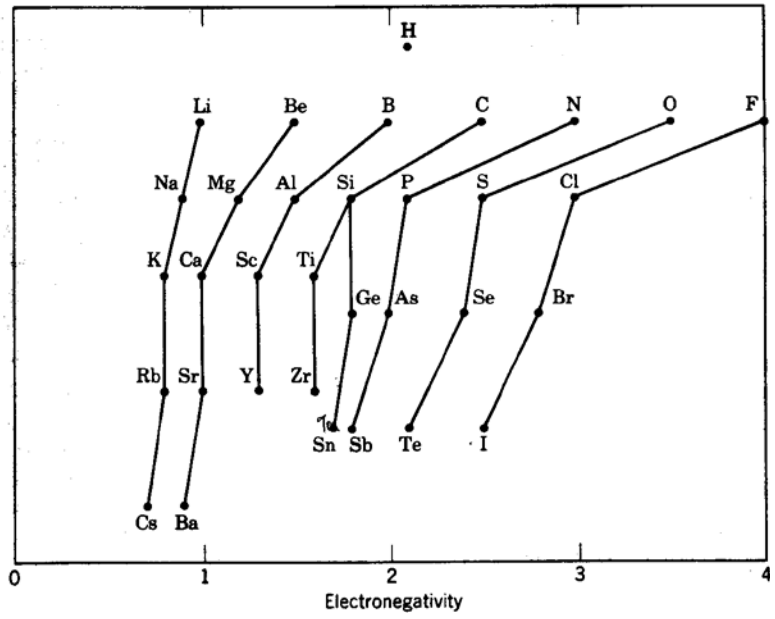
- Low electrical conductivities at low temperatures when specimens are pure

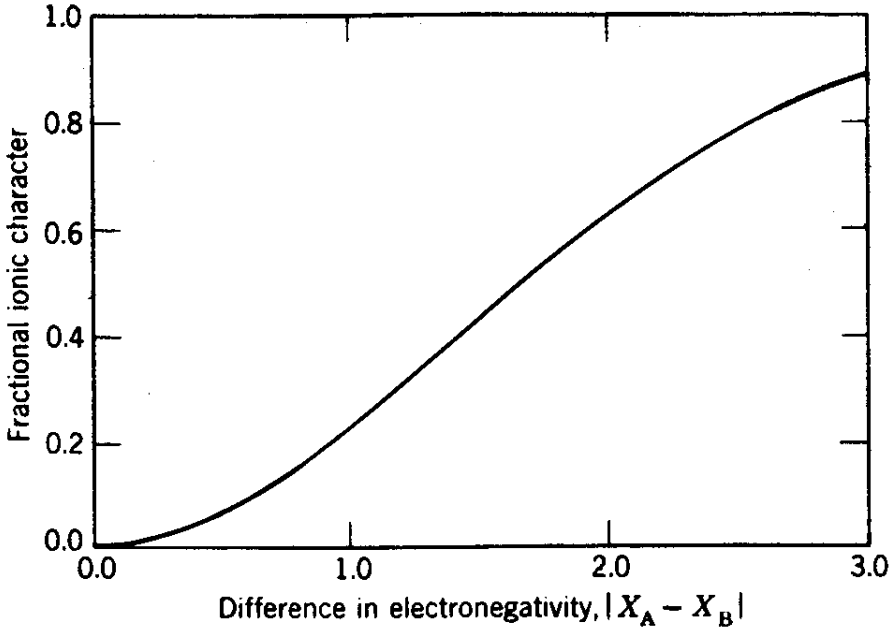
Ionic vs. Covalent Bonding

- many compounds-partially ionic and partially covalent
- degree of bond type – "electronegativity"

  - a large difference in electronegativity → largely ionic

  - similar electronegativity → largely covalent





$$\% \text{ Ionic character} = \{1 - \exp[-(0.25)(X_A - X_B)]\} \times 100$$

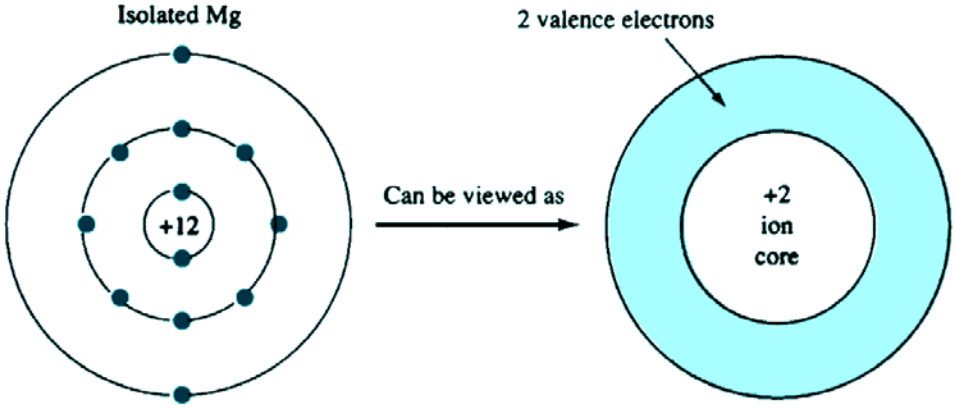
where X_A & X_B are Pauling electronegativities

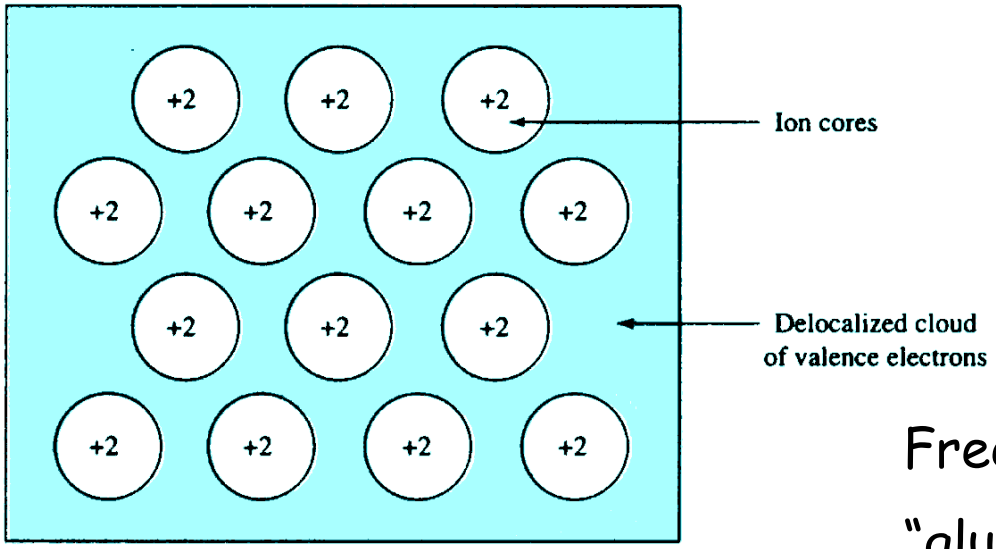
c. METALLIC

Metallic Bonding

- delocalized electron

- Arises from a sea of donated valence electrons (1, 2, or 3 from each atom)
- Primary bond for metals and their alloys

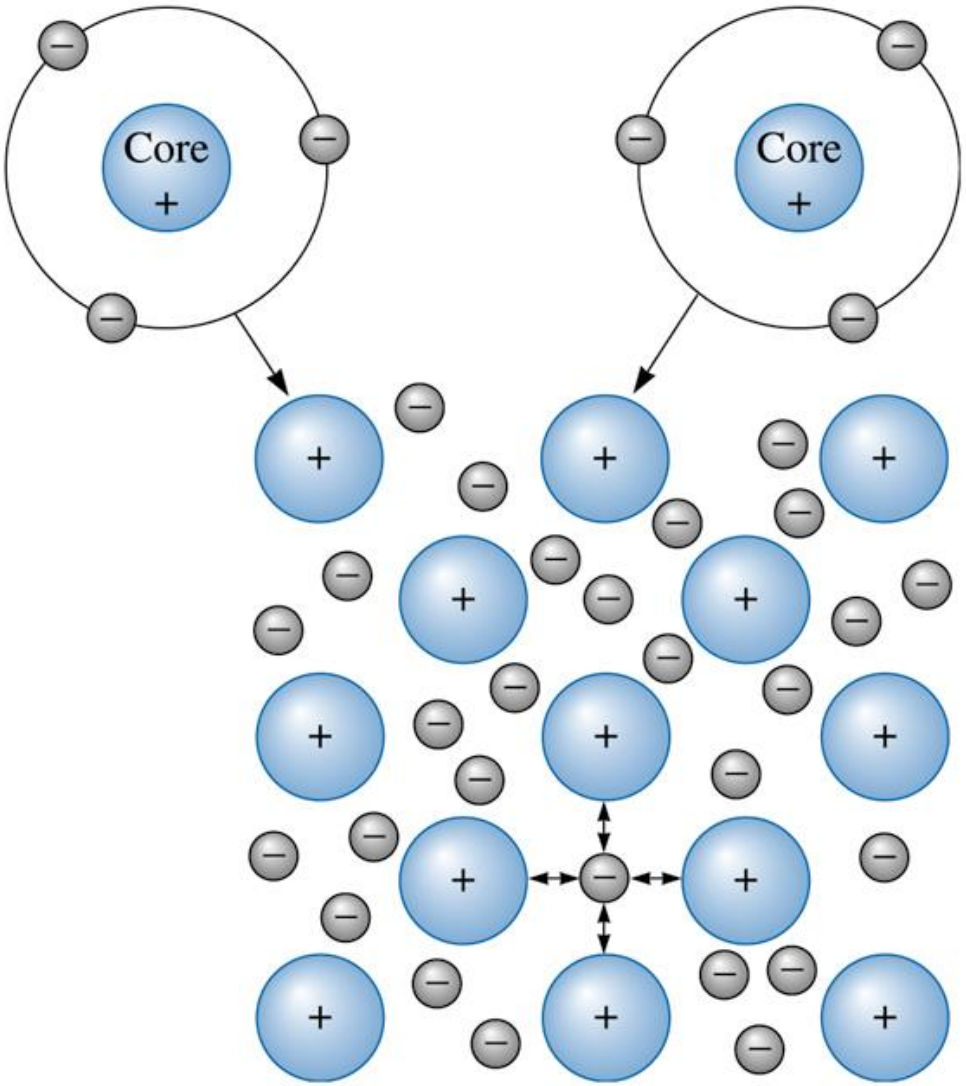




Many Mg atoms combine to form a solid metal

Free electrons act as a "glue" to hold the ion core

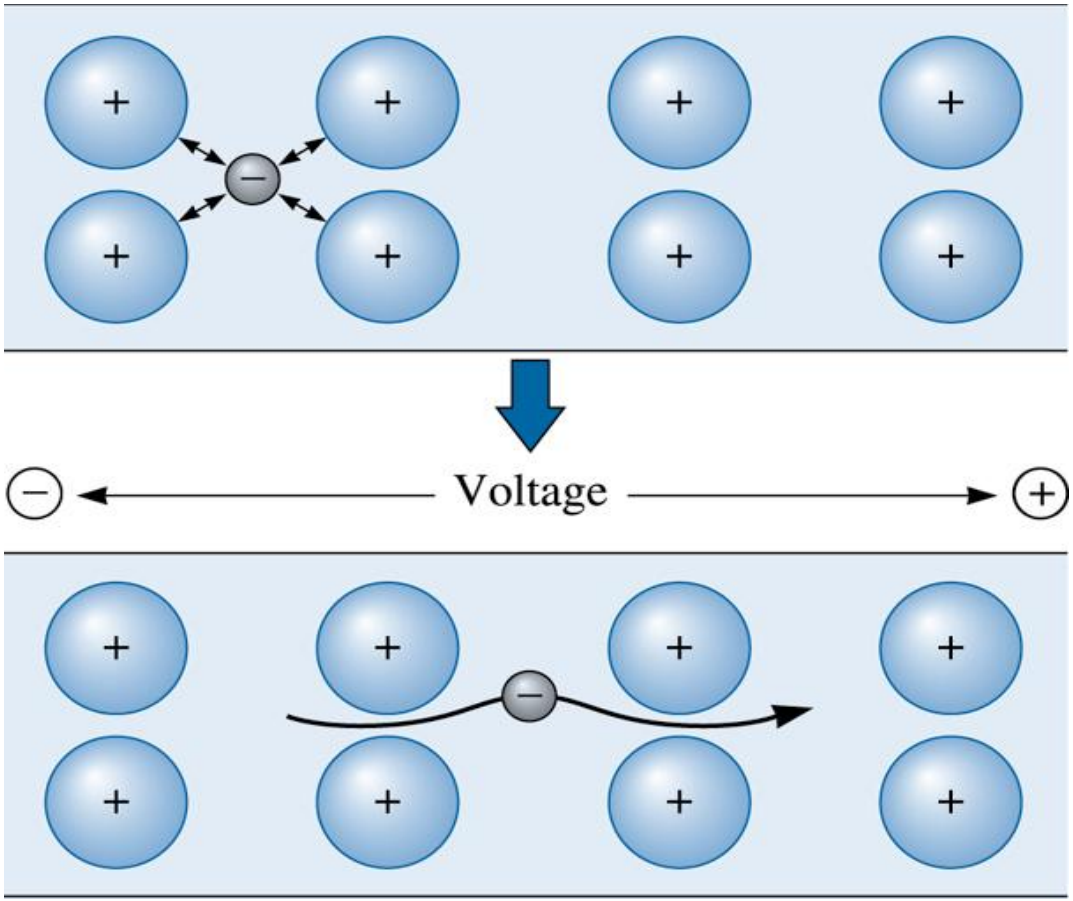
Metallic Bonding



- The metallic bond forms when atoms give up their valence electrons, which then form an electron sea.

- The positively charged atom cores are bonded by mutual attraction to the negatively charged electrons.

Metallic Bonding

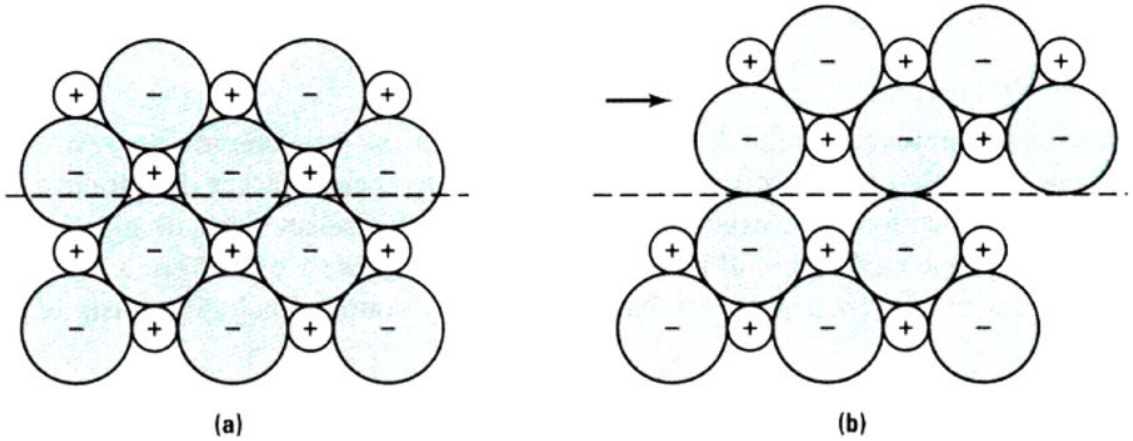


- When voltage is applied to a metal, the electrons in the electron sea can easily move and carry a current.

Metallic Bonding

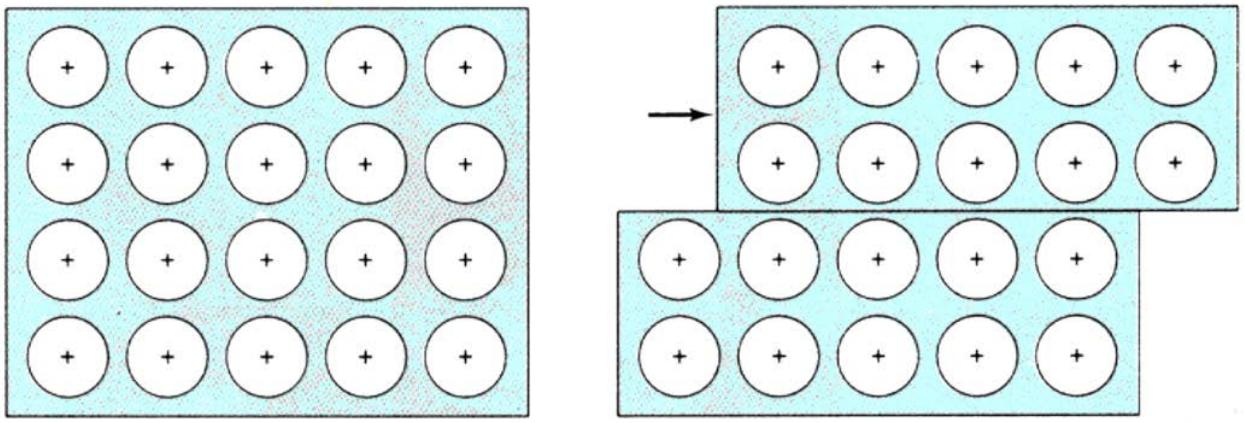
- mechanical property – What do you expect from oxides and metals?

Oxides



brittle

Metals



ductile

Primary Bonding

- Metallic Bond -- delocalized as electron cloud
- Ionic-Covalent Mixed Bonding

$$\%\ \text{ionic character} = \left[1 - exp\left\{\frac{(X_A - X_B)^2}{4}\right\}\right] \times 100\%$$

where X_A & X_B are Pauling electronegativities

Ex: MgO $\qquad X_{\text{Mg}} = 1.3, \quad X_{\text{O}} = 3.5$

$$\%\text{Ionic Character} = \left[1 - exp\left\{\frac{(3.5-1.3)^2}{4}\right\}\right] \times 100\% = 70.2\%\ \text{ionic}$$

Secondary bonding

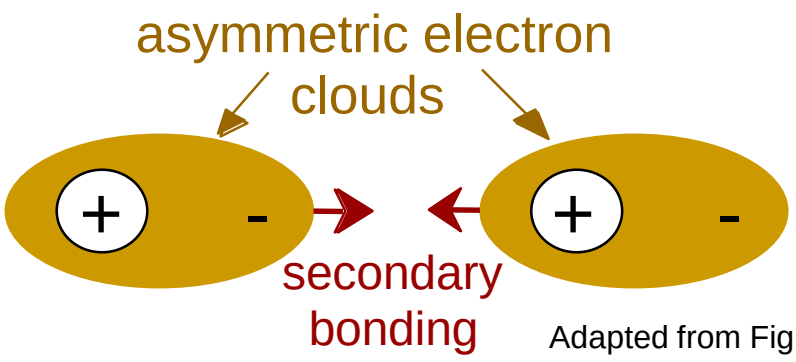
a. Van der Waals

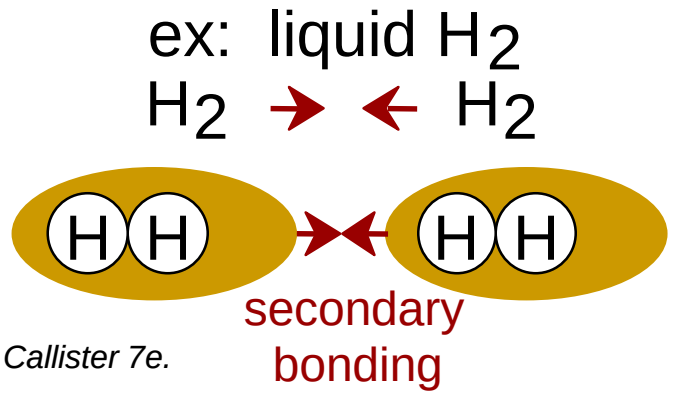
b. Hydrogen

SECONDARY BONDING 결합 E 4~30 kJ/mol

Arises from interaction between dipoles (쌍극자)

- Fluctuating dipoles





Adapted from Fig. 2.13, *Callister 7e.*

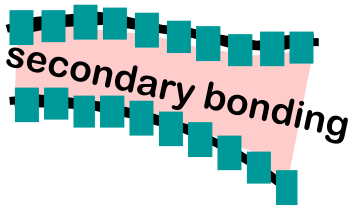
- Permanent dipoles-molecule induced

-general case:

Adapted from Fig. 2.14, *Callister 7e.*

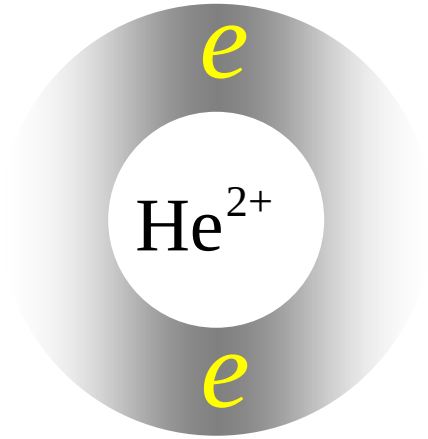
-ex: liquid HCl

-ex: polymer



secondary bonding

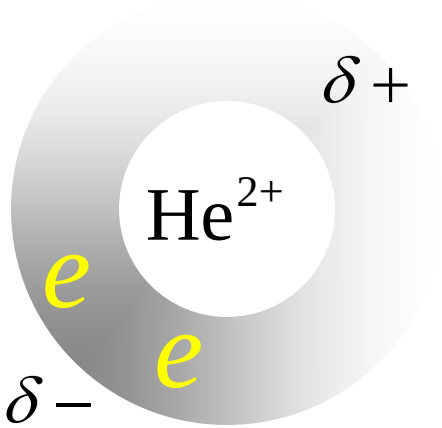
a. Van der Waals bonding (dipole bonding)



Although electrons have tendency of being separated as far as possible due to e-e repulsion, electrons are constantly in motion

It follows that electrons could get close enough to induce a "electric dipole moment" at atomistic level

This tendency is expected to be more significant as the number of electrons increases

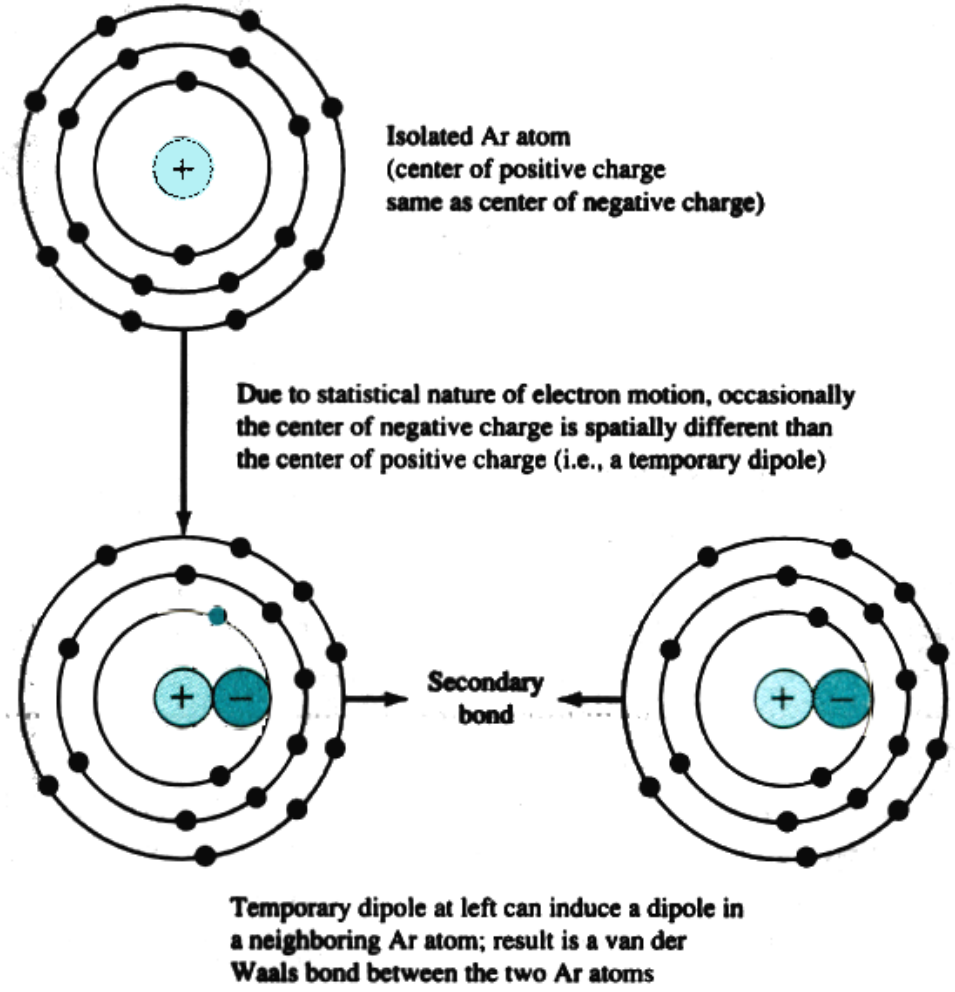


Temporal bonding due to the induced electric dipole

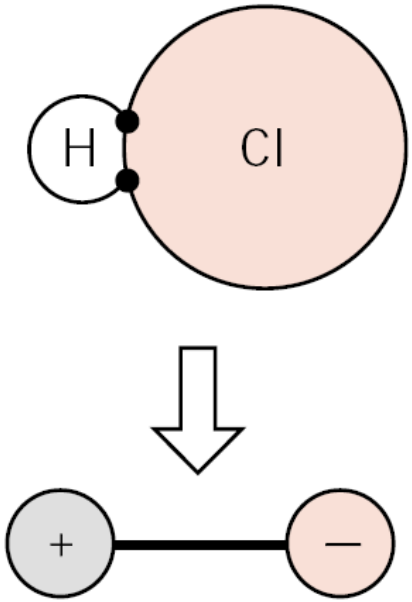
➔ van der Waals bonding

Van der Waals Bonding

(1) induced dipole

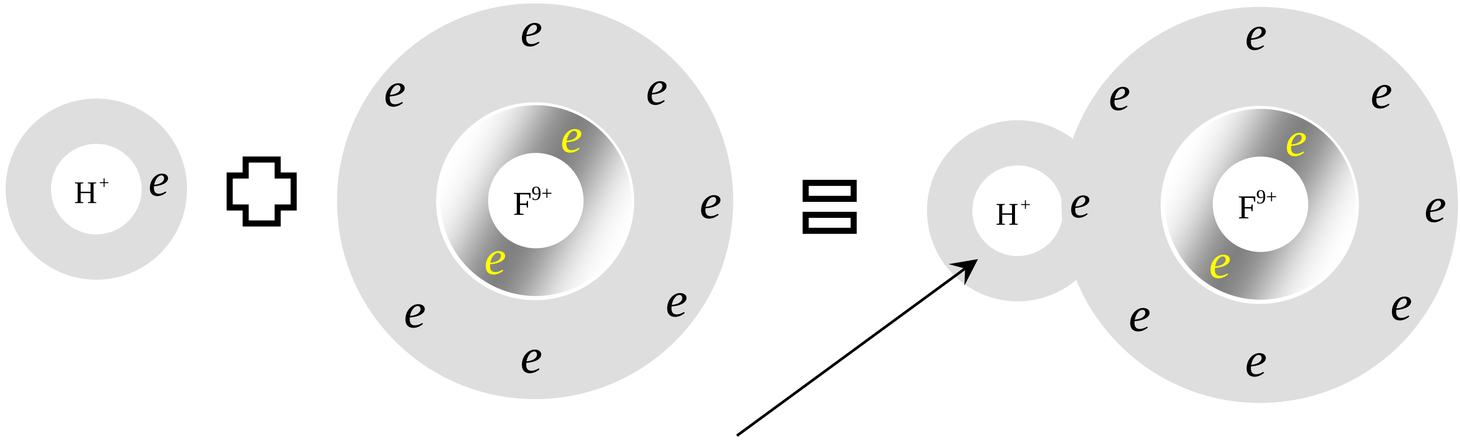


(2) permanent dipole (polar molecule)



b. Hydrogen bonding

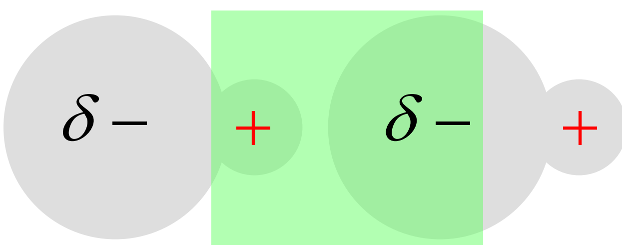
When one of the components of covalent bonding is hydrogen ...

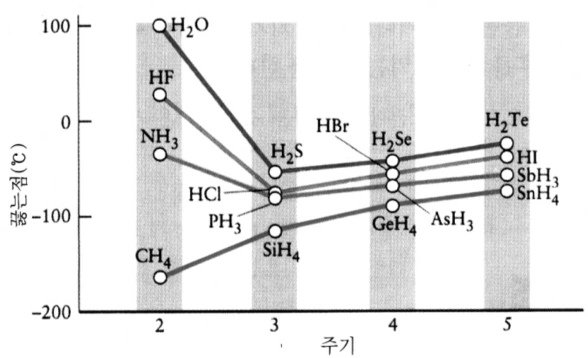


Since hydrogen atom has only one electron, there is no electron left for the formation of closed shell

→ Bare proton is exposed without being shielded by electrons ...

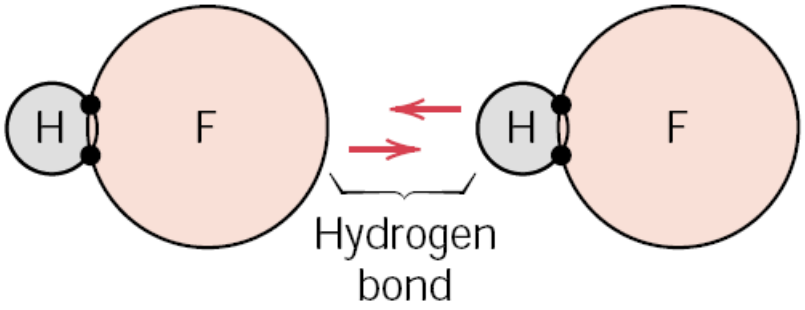
➔ Strong ionic character develops locally about hydrogen atom ...

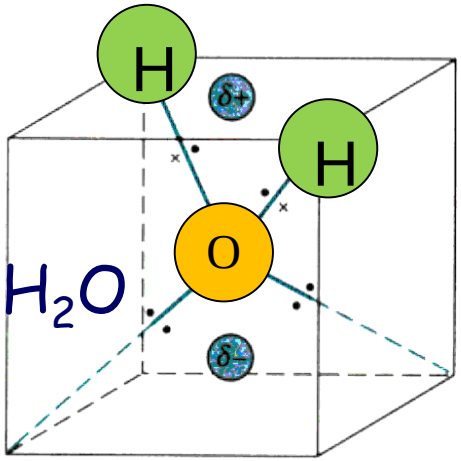


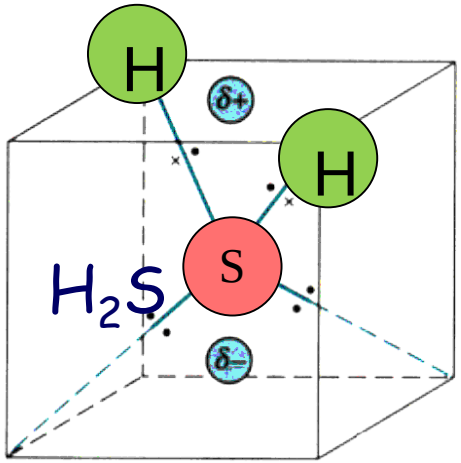


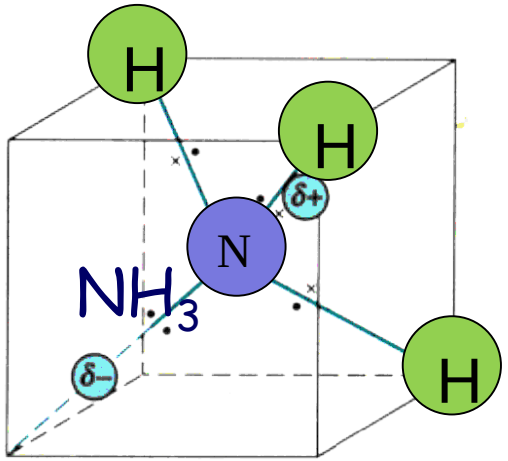
... Strong bonding develops locally ...

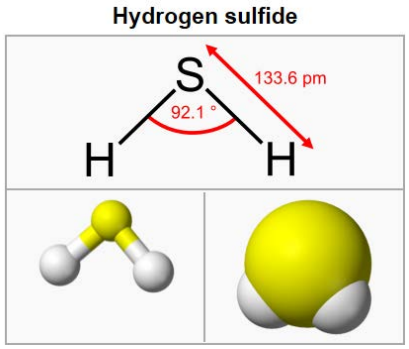
Hydrogen Bonding

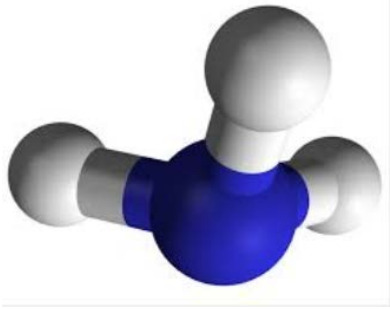








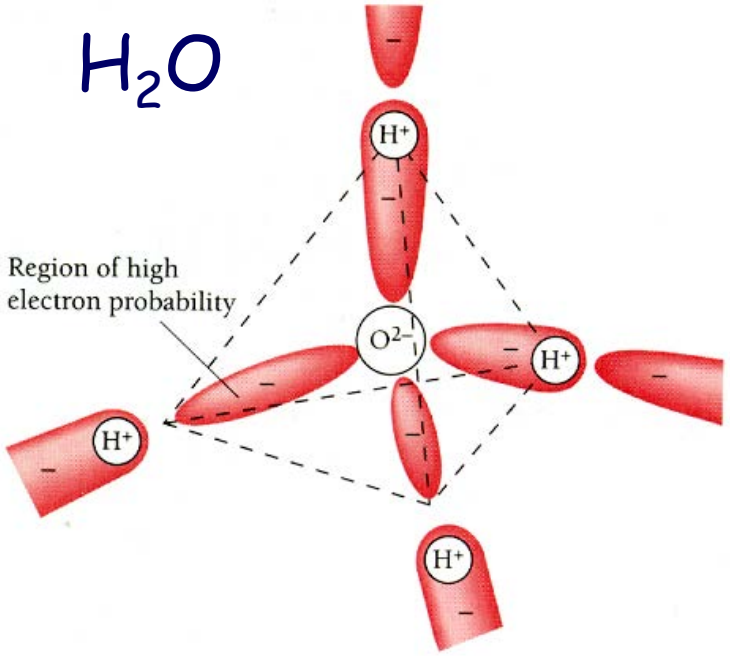




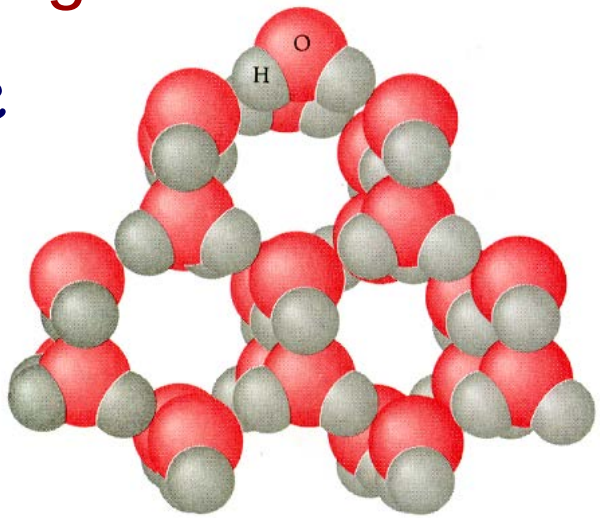
- Strongest secondary bonding
- Positively charged Hydrogen ion forms a bridge between two negatively charged ions

Hydrogen Bonding

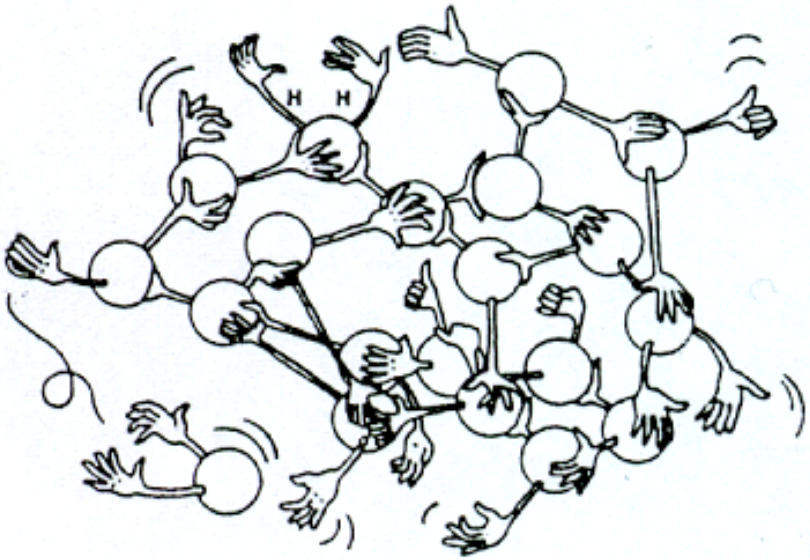
H_2O

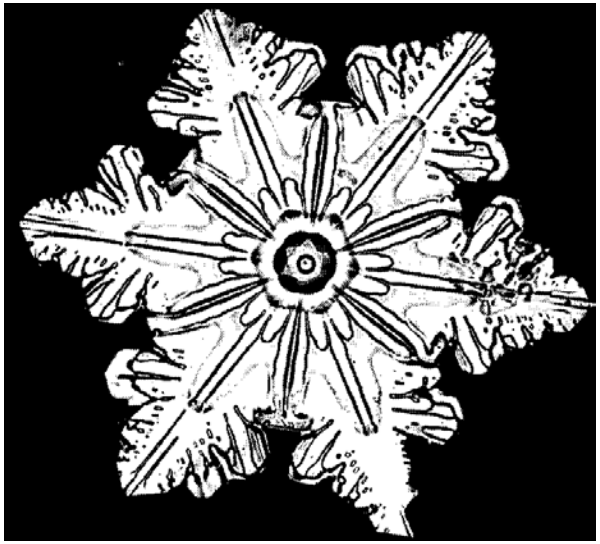


Ice



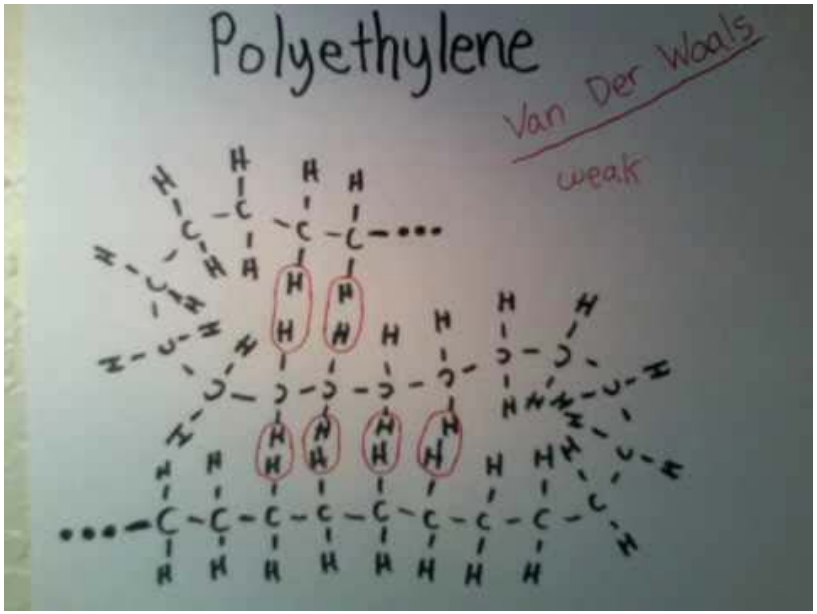
open structure
lower density

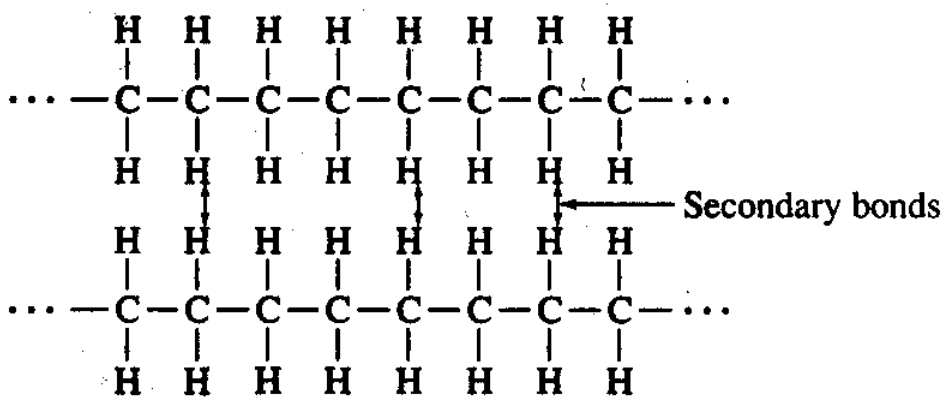




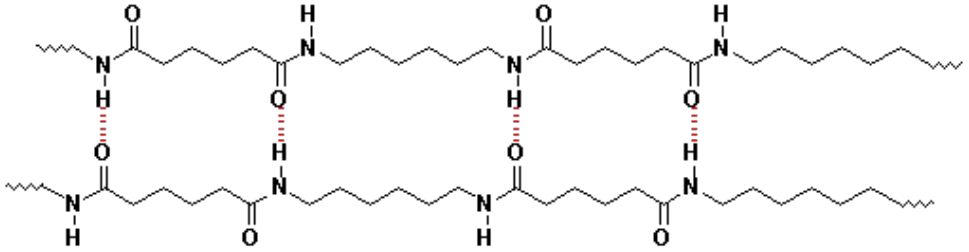
Van der Waals and Hydrogen bonding

Polyethylene

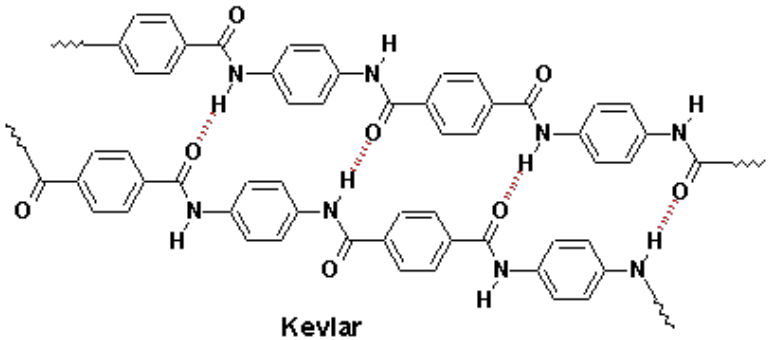




Nylon-6.6 & Kevlar



Hydrogen bonding between nylon-6,6 polymer chains



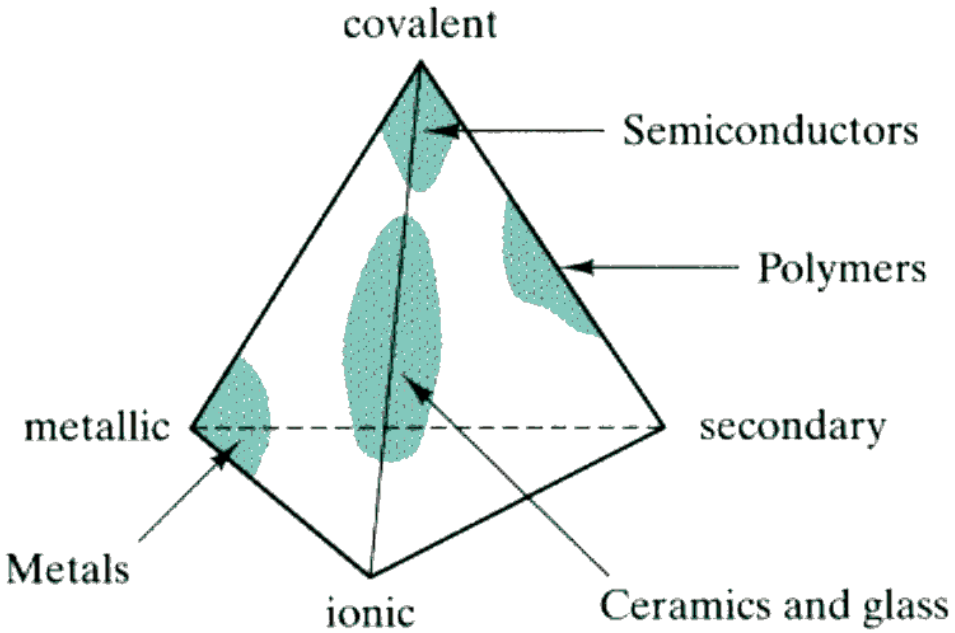
Kevlar

대부분의 분자는 공유결합에 의해 단단히 묶인 원자군→ *2차 결합에 의해 결합*

폴리머: 극히 큰 분자_**반데르발스 혹은 수소 결합**에 의해 특성 좌우

Materials-Bonding Classification

Material type	Bonding character	Example
Metal	Metallic	Iron (Fe) and the ferrous alloys
Ceramics and glasses	Ionic/covalent	Silica (SiO_2): crystalline and noncrystalline
Polymers	Covalent and secondary	Polyethylene $+C_2H_4+_n$
Semiconductors	Covalent or covalent/ionic	Silicon (Si) or cadmium sulfide (CdS)



< 실제 많은 재료는 2개 혹은 그 이상의 결합에 혼합 >

Bonding compared

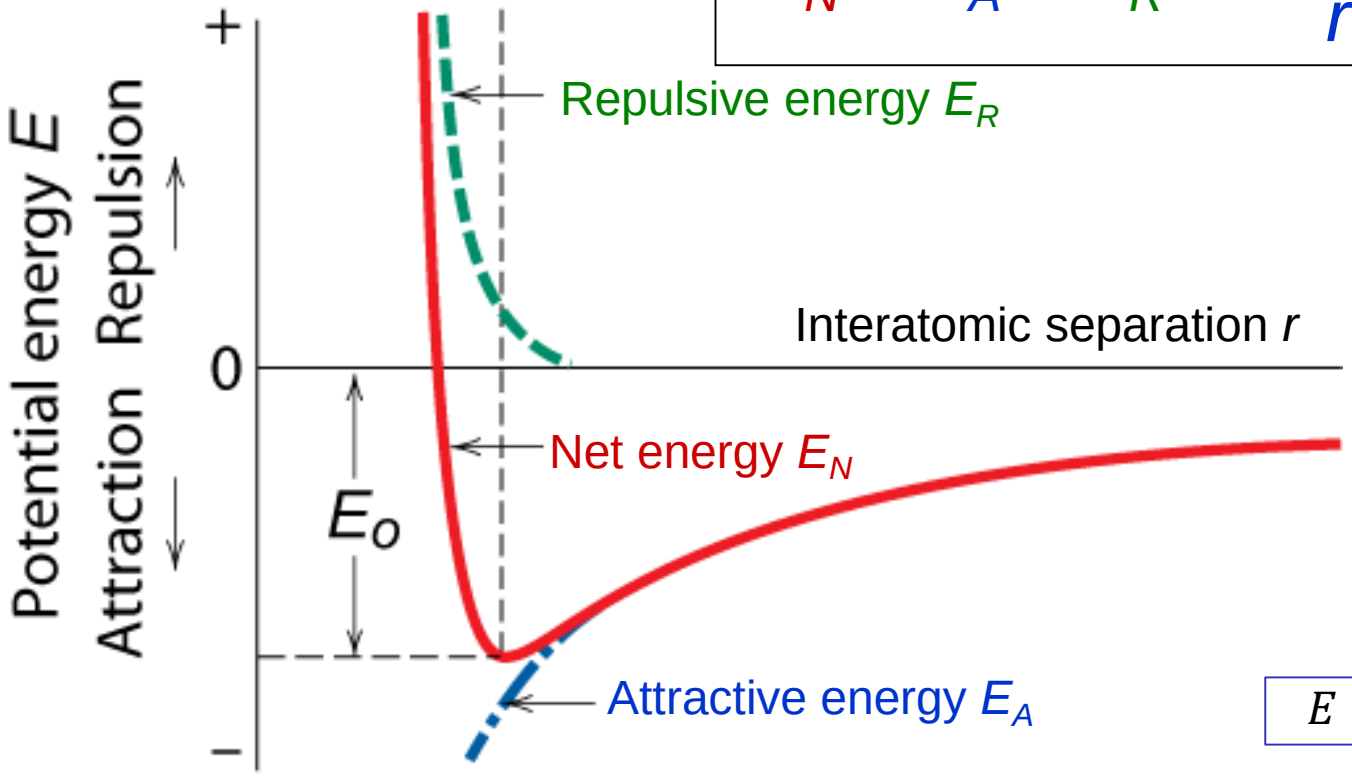
Table 2.3 Bonding Energies and Melting Temperatures for Various Substances

Bonding Type	*Substance*	*Bonding Energy*		*Melting Temperature* (°C)
		kJ/mol (*kcal/mol*)	*eV/Atom, Ion, Molecule*	
Ionic	NaCl	640 (153)	3.3	801
	MgO	1000 (239)	5.2	2800
Covalent	Si	450 (108)	4.7	1410
	C (diamond)	713 (170)	7.4	>3550
Metallic	Hg	68 (16)	0.7	−39
	Al	324 (77)	3.4	660
	Fe	406 (97)	4.2	1538
	W	849 (203)	8.8	3410
van der Waals	Ar	7.7 (1.8)	0.08	−189
	Cl_2	31 (7.4)	0.32	−101
Hydrogen	NH_3	35 (8.4)	0.36	−78
	H_2O	51 (12.2)	0.52	0

Bonding Energy : potential well concept

- Energy – minimum energy most stable
  - Energy balance of attractive and repulsive terms

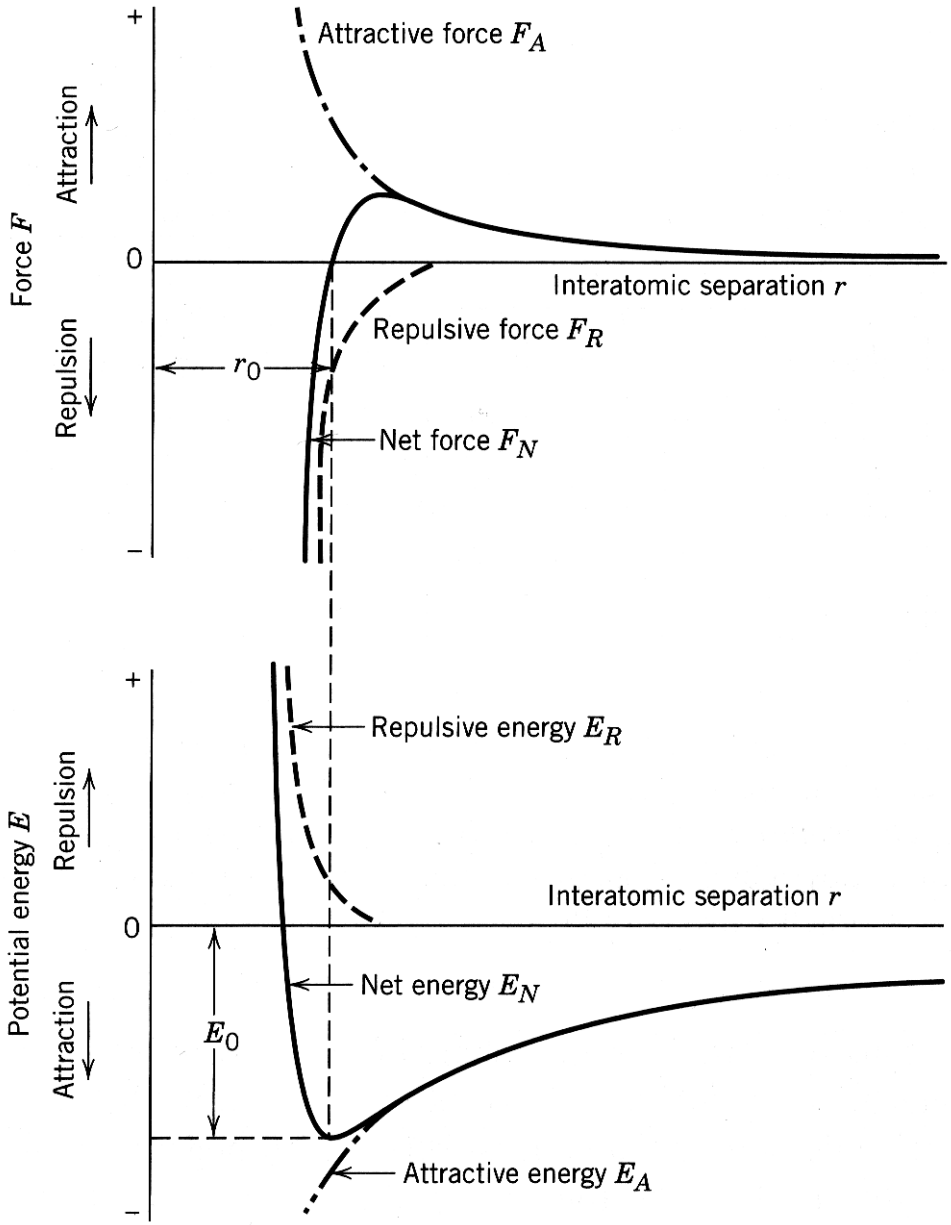
$$E_N = E_A + E_R = -\frac{A}{r} - \frac{B}{r^n}$$



$$E = \int F\, dr$$

Adapted from Fig. 2.8(b), *Callister 7e.*

Bonding Forces & Energies



$$F_N = F_A + F_R = 0$$

$$E_N = E_A + E_R \quad F = dE/dr$$

- Covalent bonding

F_A **: nucleus to electrons**

F_R **: nucleus to nucleus**

: electrons to electrons

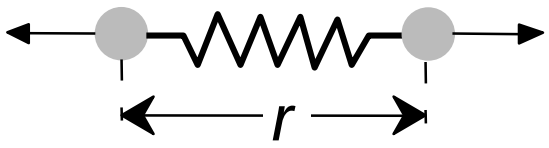
- Ionic bonding

F_A **: electrostatic attraction between unlike ions**

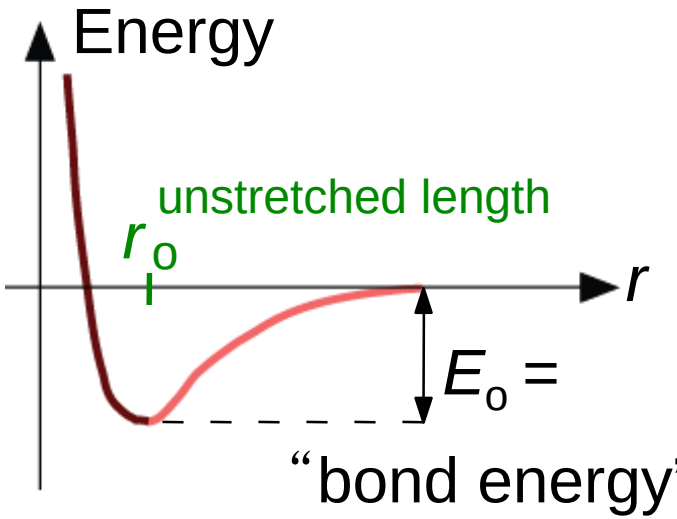
F_R **: closed shell overlapping**

(a) Properties From Bonding: T_m

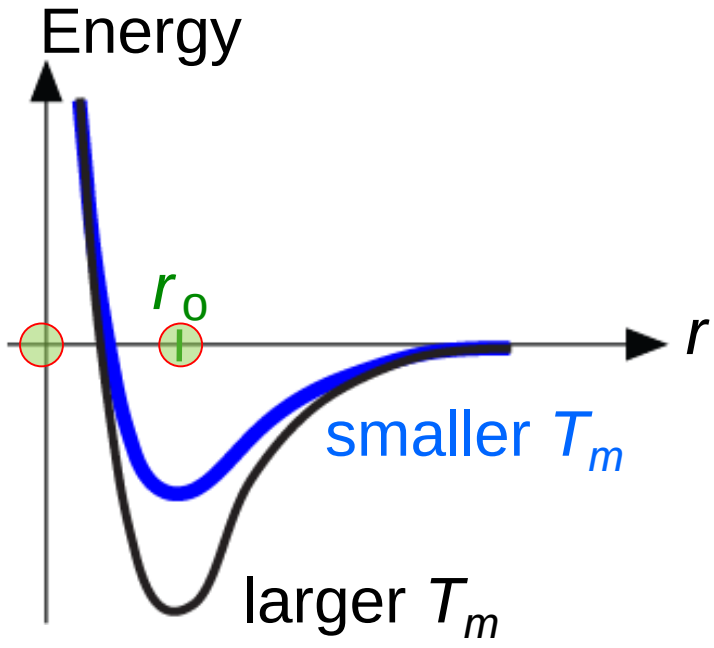
- Bond length, r



- Bond energy, E_o



- Melting Temperature, T_m



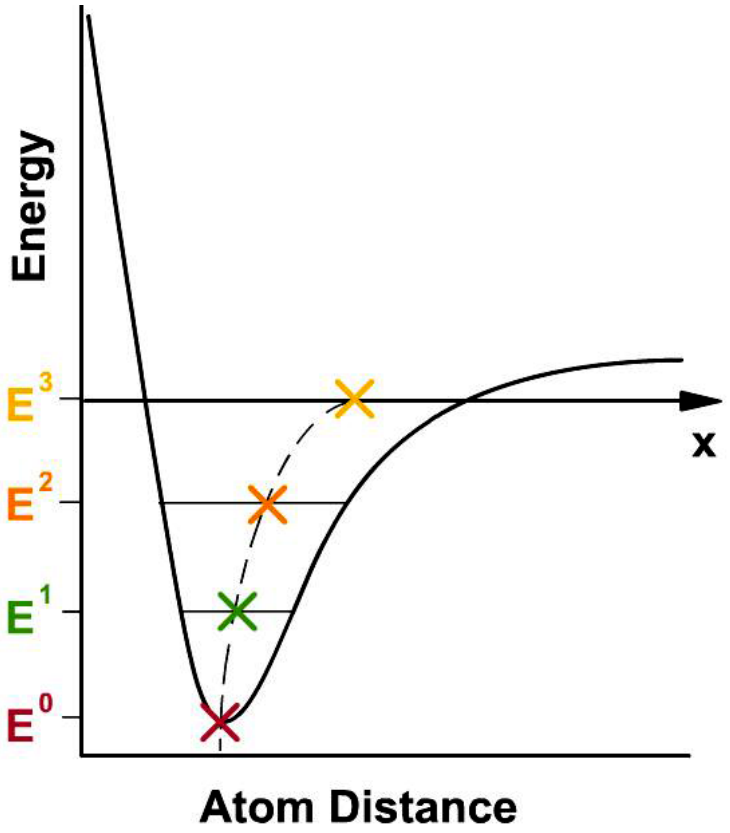
T_m is larger if E_o is larger.

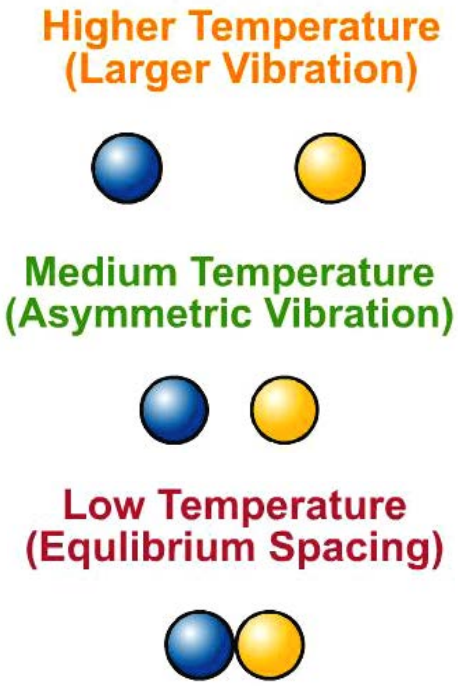
두원자를 무한대로 분리시키기 위해 필요한 에너지

(b) Properties From Bonding : α

Thermal Expansion

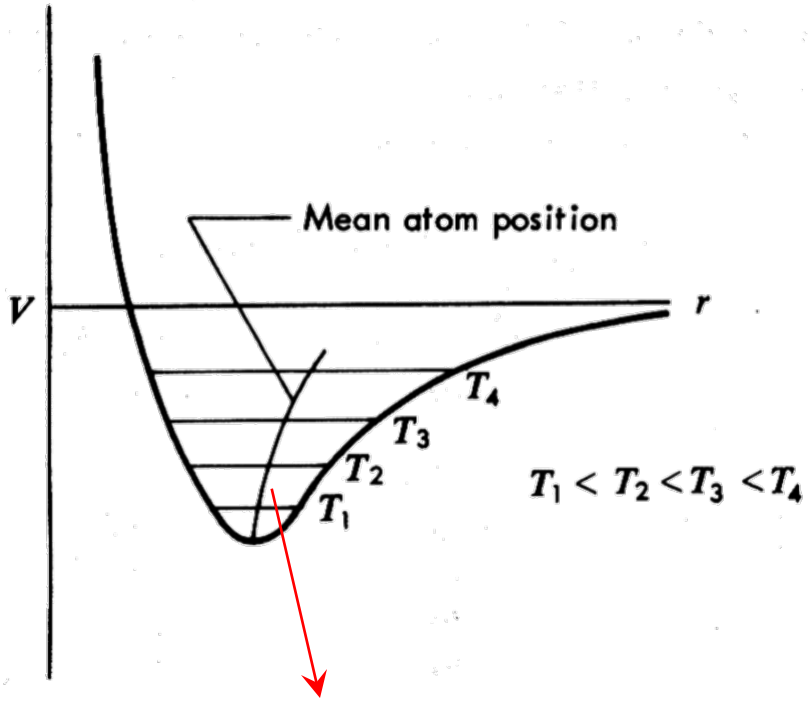
- Thermal expansion ← asymmetric nature of the energy well
- Broad well (generally more asymmetric) → larger expansion

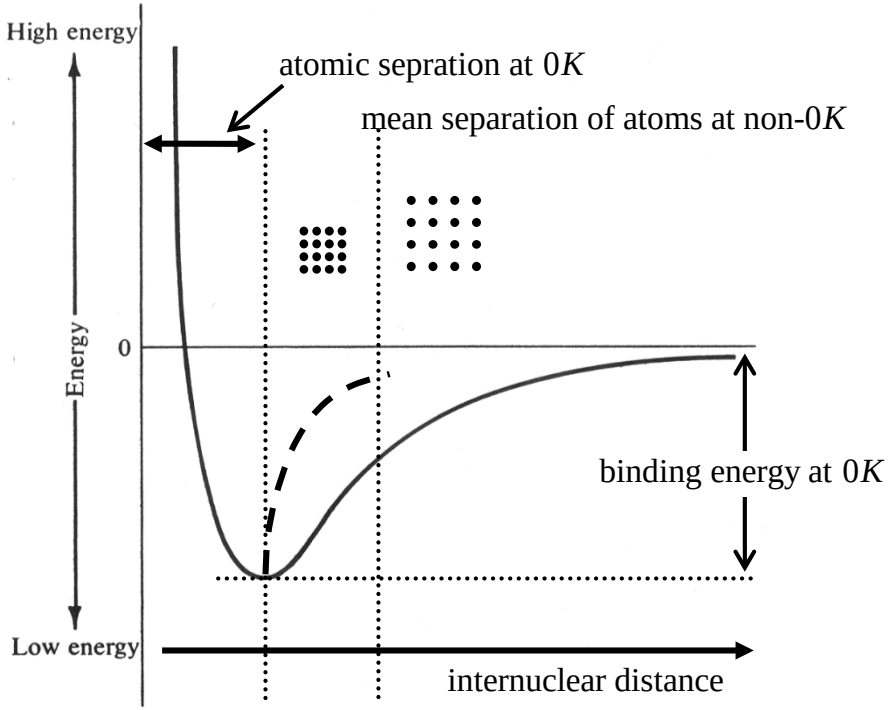




Properties From Bonding : α

Temperature supplies thermal energy into solids → thermal vibration (phonon)

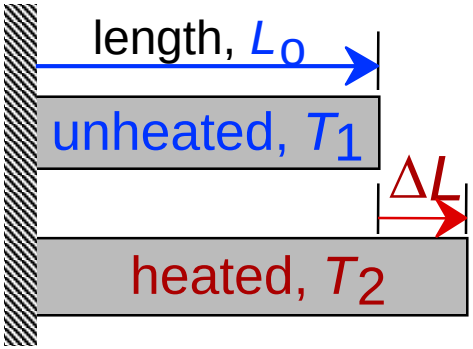




Slope is related to the thermal expansion coefficient of materials

Properties From Bonding : α

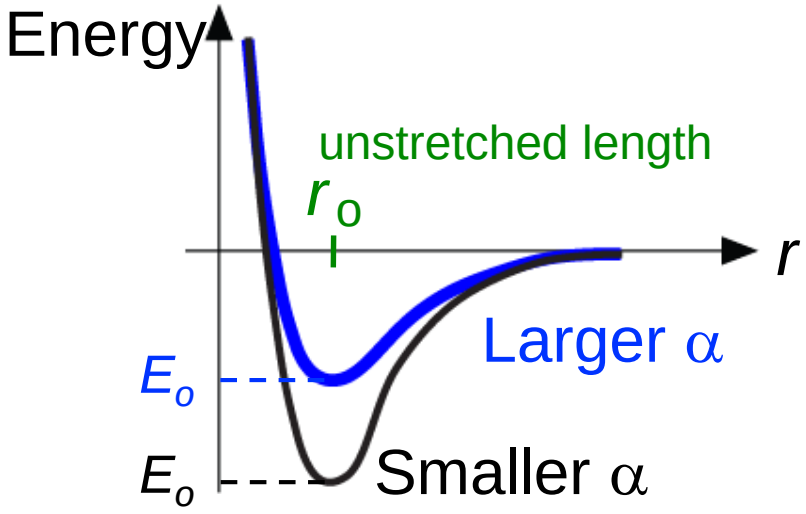
- Coefficient of thermal expansion, α



coeff. thermal expansion

$$\frac{\Delta L}{L_o} = \alpha\,(T_2 - T_1)$$

- α ~ symmetry at r_o



α is larger if E_o is smaller.

Bonding

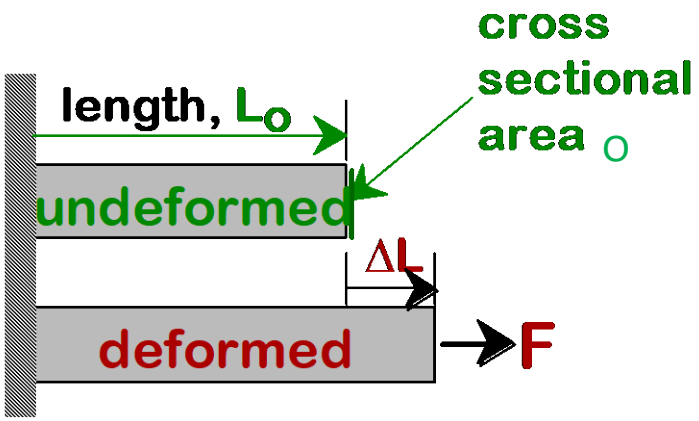
Primary bonding

Secondary

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

(c) Properties from Bonding: E

- Elastic (Young's) modulus, E (y)



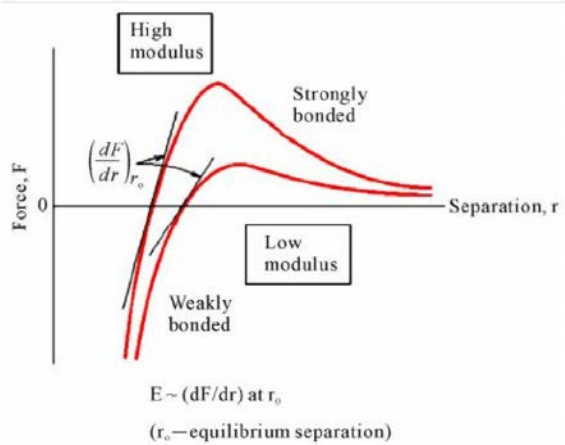
Elastic modulus

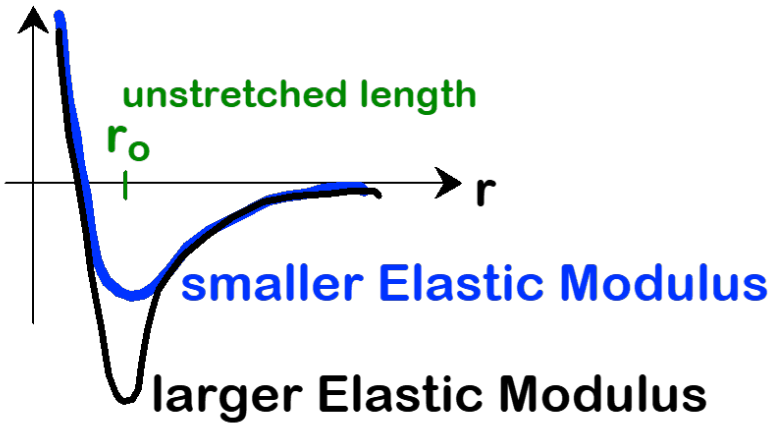
$$\frac{F}{A_o} = E\frac{\Delta L}{L_o}$$

$$\sigma = E\varepsilon$$

- E ~ curvature at r_o (the bottom of the well)

$$Y \sim \left(\frac{d^2E}{dr^2}\right)_{r_o}$$





E is larger if E_o is larger

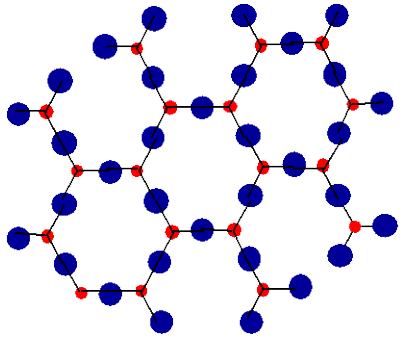
Potential Well Concept

Material	Elastic Modulus (10^6 psi)	Elastic Modulus (10^{11} dynes/cm^2)	Linear Thermal Expansion Coefficient, α (length/length·°C)
Diamond	114	77.5	1.2×10^{-6}
W_2C	90	61.2	$\approx 7.0 \times 10^{-6}$
W	56.5	38.4	4.4×10^{-6}
Al_2O_3	50	34.0	8.7×10^{-6}
MgO	40	27.2	$\approx 10.0 \times 10^{-6}$
Ni	30	20.4	13.0×10^{-6}
Si	29	19.7	7.6×10^{-6}
Ge	23	15.7	—
LiF	19	12.9	—
Cu	17	11.5	16.8×10^{-6}
SiO_2	10	6.8	8.0×10^{-6}
Mg	6.3	4.3	26.0×10^{-6}
NaCl	4.7	3.7	40.4×10^{-6}
Polystyrene	0.4	0.27	$\approx 79 \times 10^{-6}$
Nylon	0.4	0.27	$\approx 100 \times 10^{-6}$
Polytetrafluorethylene	0.06	0.041	$\approx 100 \times 10^{-6}$
Polyethylene	0.02	0.014	$\approx 300 \times 10^{-6}$
Natural rubber	10^{-3}–10^{-2}	$\approx 7 \times 10^{-4}$	$\approx 650 \times 10^{-6}$
		7×10^{-3}	

MATERIALS AND PACKING

Crystalline materials...

- atoms pack in periodic, 3D arrays
- typical of: -metals
  -many ceramics
  -some polymers



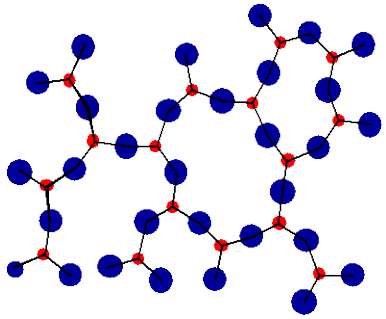
crystalline SiO_2

Adapted from Fig. 3.18(a), *Callister 6e.*

• Si • Oxygen

Noncrystalline materials...

- atoms have no periodic packing
- occurs for: -complex structures
  -rapid cooling



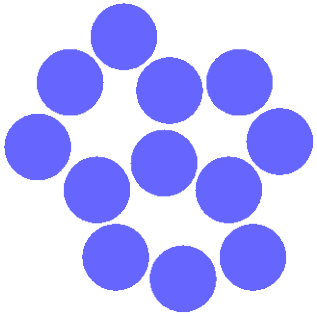
noncrystalline SiO_2

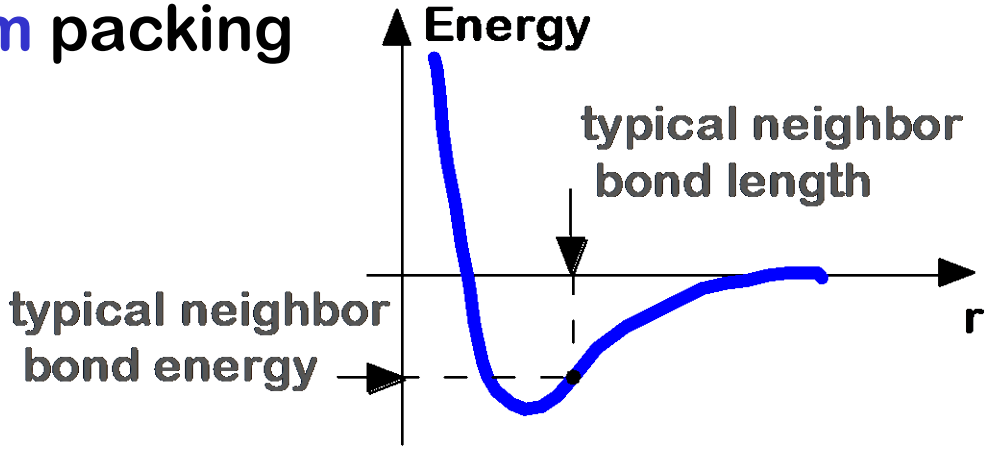
Adapted from Fig. 3.18(b), *Callister 6e.*

"Amorphous" = Noncrystalline

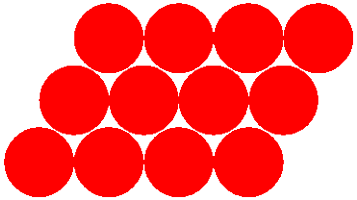
ENERGY AND PACKING

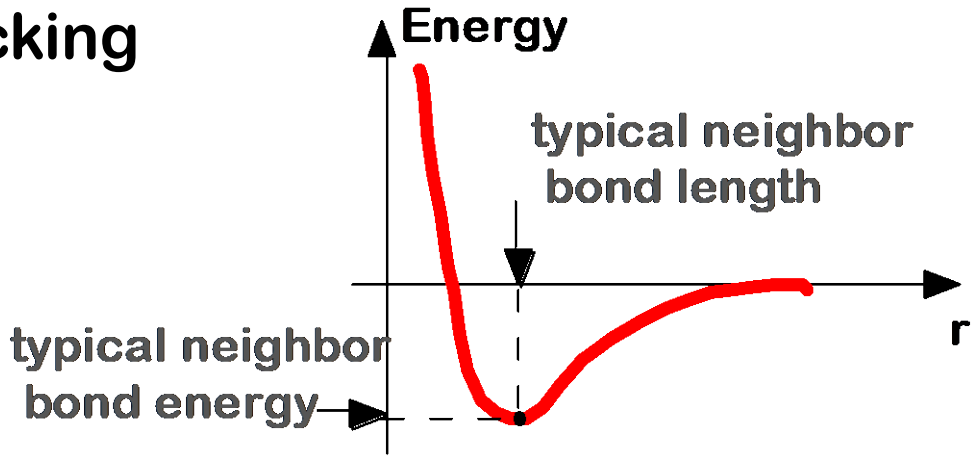
- Non dense, random packing





- Dense, regular packing





Dense, regular-packed structures tend to have lower energy.

SUMMARY: BONDING

Type	Bond Energy	Comments
Ionic	Large!	Nondirectional (ceramics)
Covalent	Variable large-Diamond small-Bismuth	Directional semiconductors, ceramics polymer chains)
Metallic	Variable large-Tungsten small-Mercury	Nondirectional (metals)
Secondary	smallest	Directional inter-chain (polymer) inter-molecular

Summary: Properties from Bonds

Ceramics

(Ionic & covalent bonding):

Large bond energy

large T_m
large E
small α

Metals

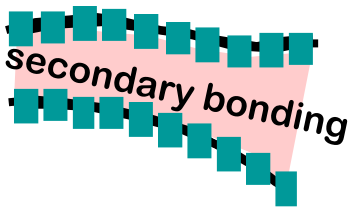
(Metallic bonding):

Variable bond energy

moderate T_m
moderate E
moderate α

Polymers

(Covalent & Secondary):



Directional Properties

Secondary bonding dominates

small T_m
small E
large α

2020 Fall

Introduction to Materials Science and Engineering

09. 10. 2020

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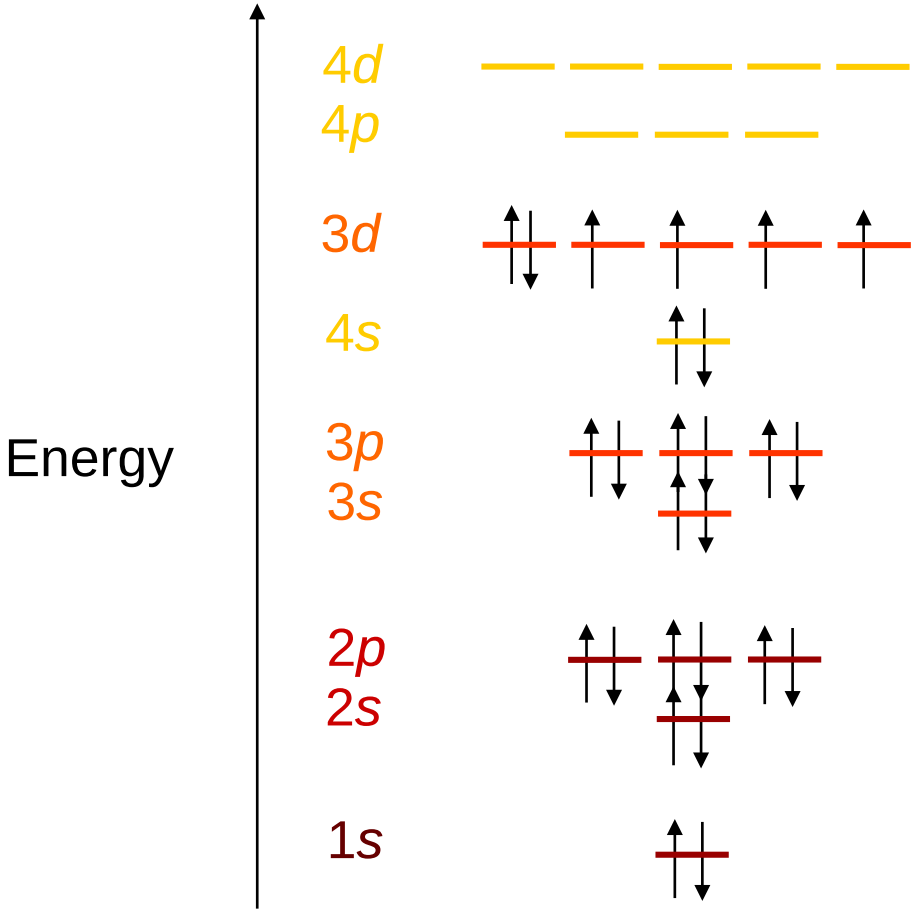
Electronic Configurations

ex: Fe - atomic # = 26 $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^6$ $4s^2$

= 26

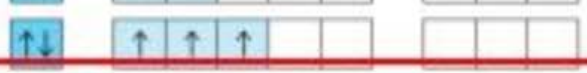
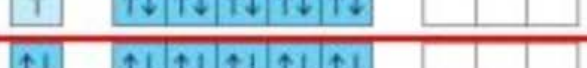
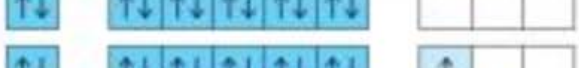
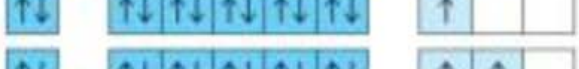
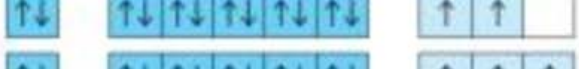
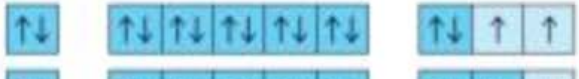
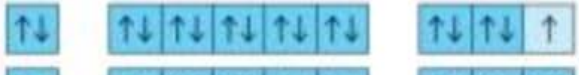


Valence Electrons

(전자들이 에너지가 가장 낮은 상태에 있는 바닥상태에서 반응에 참여할 수 있는 전자)

Adapted from Fig. 2.4, *Callister 7e.*

표 8.3 4주기 원소들의 부분적인 궤도 그림과 전자 배치*

원자번호	원소	부분 궤도 그림(3s, 3p, 3d 부준위만)	총 전자 배치	요약된 전자 배치
		4s 3d 4p		
19	K		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^1$	[Ar] $4s^1$
20	Ca		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2$	[Ar] $4s^2$
21	Sc		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^1$	[Ar] $4s^2 3d^1$
22	Ti		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^2$	[Ar] $4s^2 3d^2$
23	V		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^3$	[Ar] $4s^2 3d^3$
24	Cr		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^1 3d^5$	[Ar] $4s^1 3d^5$
25	Mn		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^5$	[Ar] $4s^2 3d^5$
26	Fe		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^6$	[Ar] $4s^2 3d^6$
27	Co		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^7$	[Ar] $4s^2 3d^7$
28	Ni		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^8$	[Ar] $4s^2 3d^8$
29	Cu		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^1 3d^{10}$	[Ar] $4s^1 3d^{10}$
30	Zn		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^{10}$	[Ar] $4s^2 3d^{10}$
31	Ga		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^{10} 4p^1$	[Ar] $4s^2 3d^{10} 4p^1$
32	Ge		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^{10} 4p^2$	[Ar] $4s^2 3d^{10} 4p^2$
33	As		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^{10} 4p^3$	[Ar] $4s^2 3d^{10} 4p^3$
34	Se		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^{10} 4p^4$	[Ar] $4s^2 3d^{10} 4p^4$
35	Br		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^{10} 4p^5$	[Ar] $4s^2 3d^{10} 4p^5$
36	Kr		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^{10} 4p^6$	[Ar] $4s^2 3d^{10} 4p^6$

* 색으로 표시된 것은 마지막 전자가 더해진 부준위를 표시한다.

SURVEY OF ELEMENTS

- Most elements: Electron configuration not stable.

Element	Atomic #	Electron configuration	
Hydrogen	1	$1s^1$	
Helium	2	$1s^2$	(stable)
Lithium	3	$1s^2 2s^1$	
Beryllium	4	$1s^2 2s^2$	
Boron	5	$1s^2 2s^2 2p^1$	
Carbon	6	$1s^2 2s^2 2p^2$	
...		...	
Neon	10	$1s^2 2s^2 2p^6$	(stable)
Sodium	11	$1s^2 2s^2 2p^6 3s^1$	
Magnesium	12	$1s^2 2s^2 2p^6 3s^2$	
Aluminum	13	$1s^2 2s^2 2p^6 3s^2 3p^1$	
...		...	
Argon	18	$1s^2 2s^2 2p^6 3s^2 3p^6$	(stable)
...	...	...	
Krypton	36	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$	(stable)

Adapted from Table 2.2, *Callister 7e.*

- Why? Valence (outer) shell usually not filled completely.

Contents for previous class

Atomic Bonding in Solids : an attempt to fill electron shells

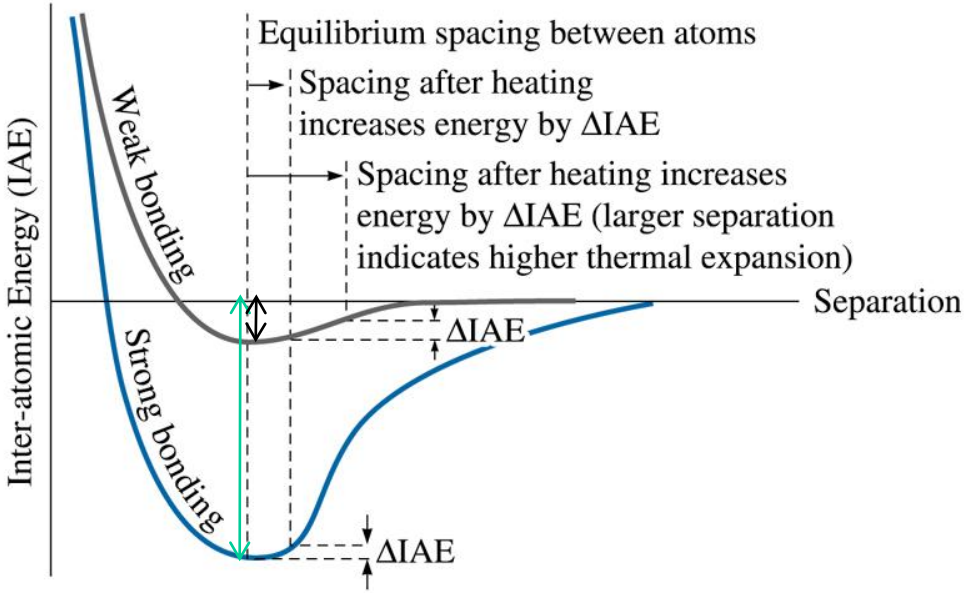
a. Primary bonding

(1) Ionic bonds
(2) Covalent bonds
(3) Metallic bonds

b. Secondary bonding

(1) Van der Waals
(2) Hydrogen bonding

c. Properties From Bonding



If E_o is larger,

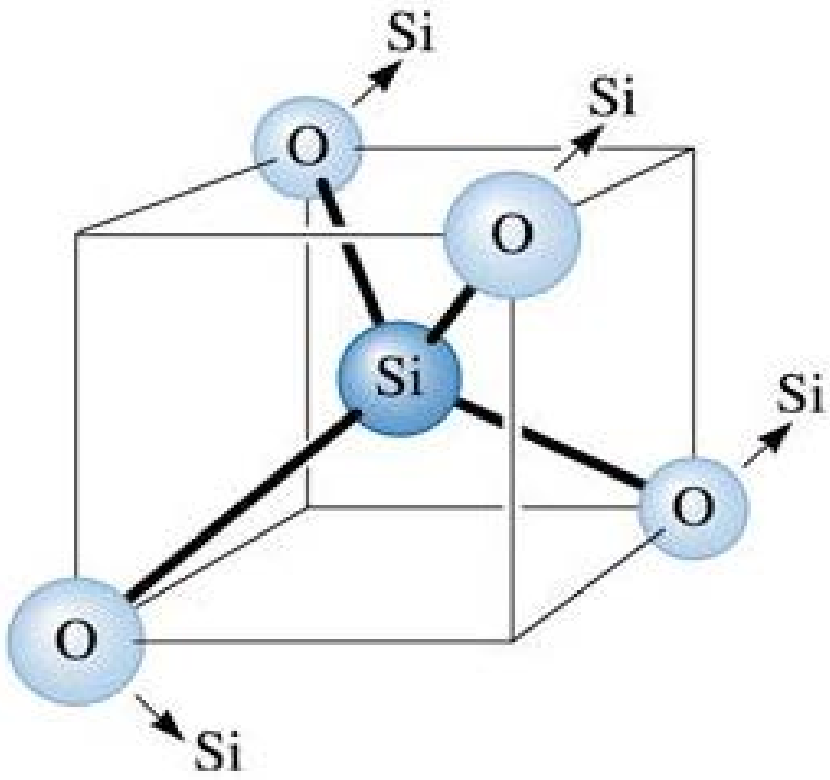
T_m (melting temp.→ Broken Bonds), E (elastic modulus), ((possibly))

Yield strength is larger,

but α is smaller.

(thermal expansion coefficient)

Covalent Bonding



VS.

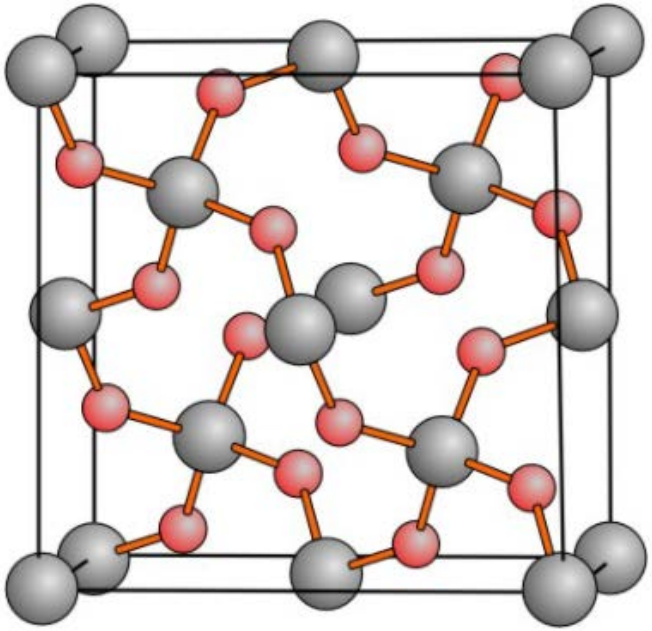


Figure 8.26: Structure of High Cristobalite, a Form of Quartz

- **The tetrahedral structure of silica (SiO_2), which contains covalent bonds between silicon and oxygen atoms**

Covalent Bonding: Bond Hybrization

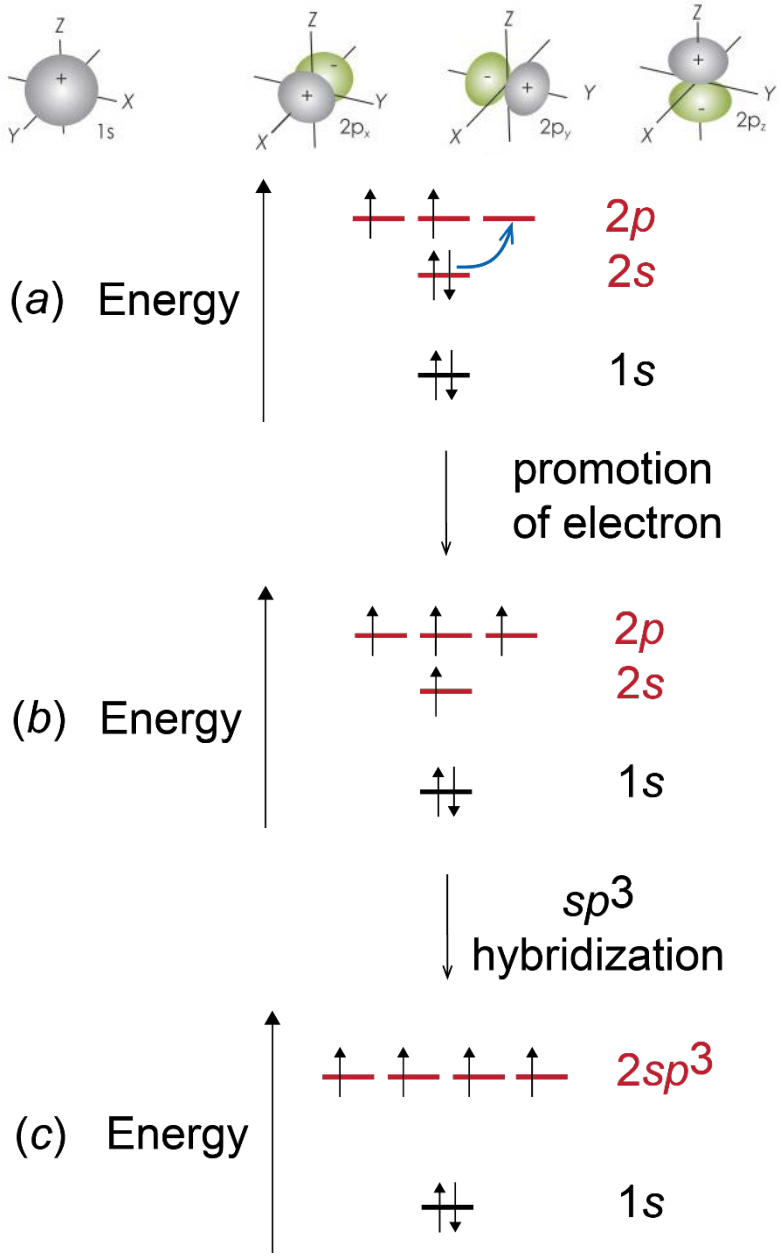


Fig. 2.13, *Callister & Rethwisch 10e.*

- Carbon can form sp^3 hybrid orbitals

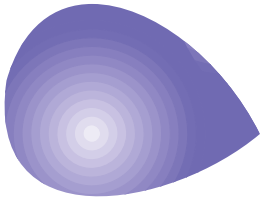


Fig. 2.14, *Callister & Rethwisch 10e.*
(Adapted from J.E. Brady and F. Senese, *Chemistry: Matter and Its Changes*, 4th edition. Reprinted with permission of John Wiley and Sons, Inc.)

Covalent Bonding (cont.)

Hybrid sp^3 bonding involving carbon

Example: CH_4

C: each has 4 valence electrons, needs 4 more

H: each has 1 valence electron, needs 1 more

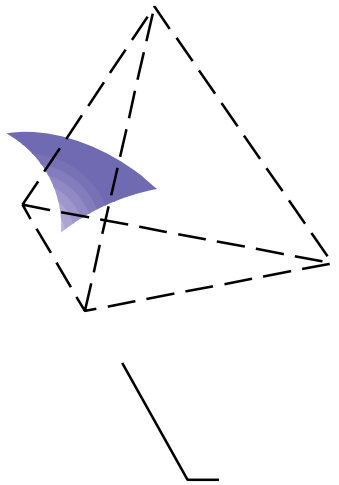
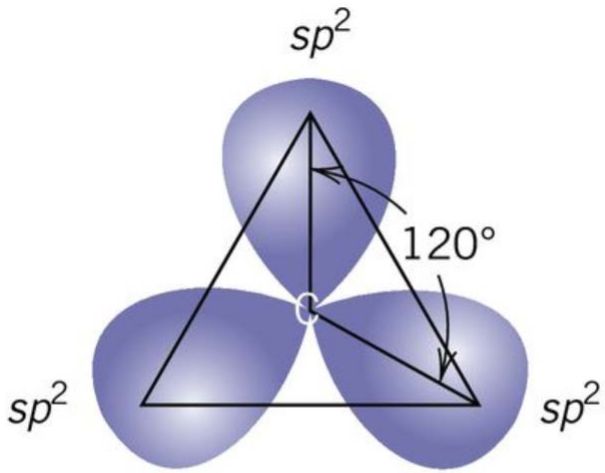
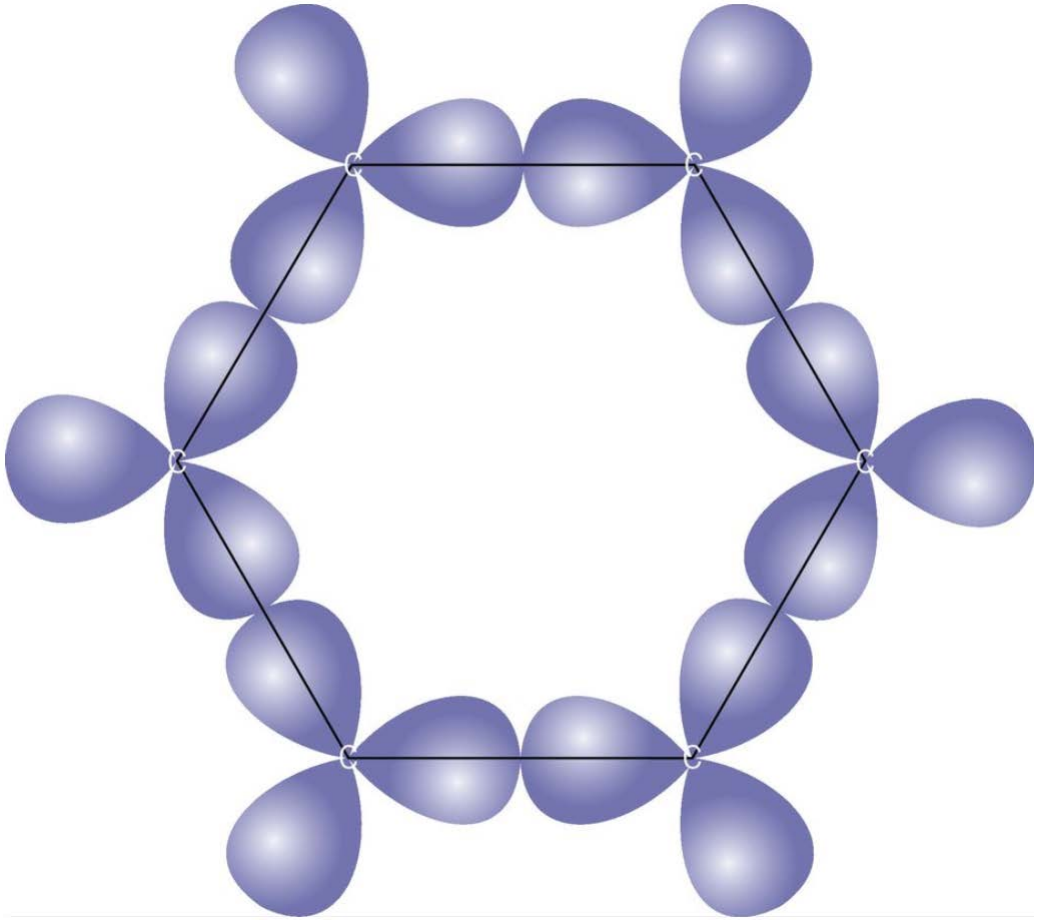


Fig. 2.15, *Callister & Rethwisch 10e.* (Adapted from J.E. Brady and F. Senese, *Chemistry: Matter and Its Changes*, 4th edition. Reprinted with permission of John Wiley and Sons, Inc.)

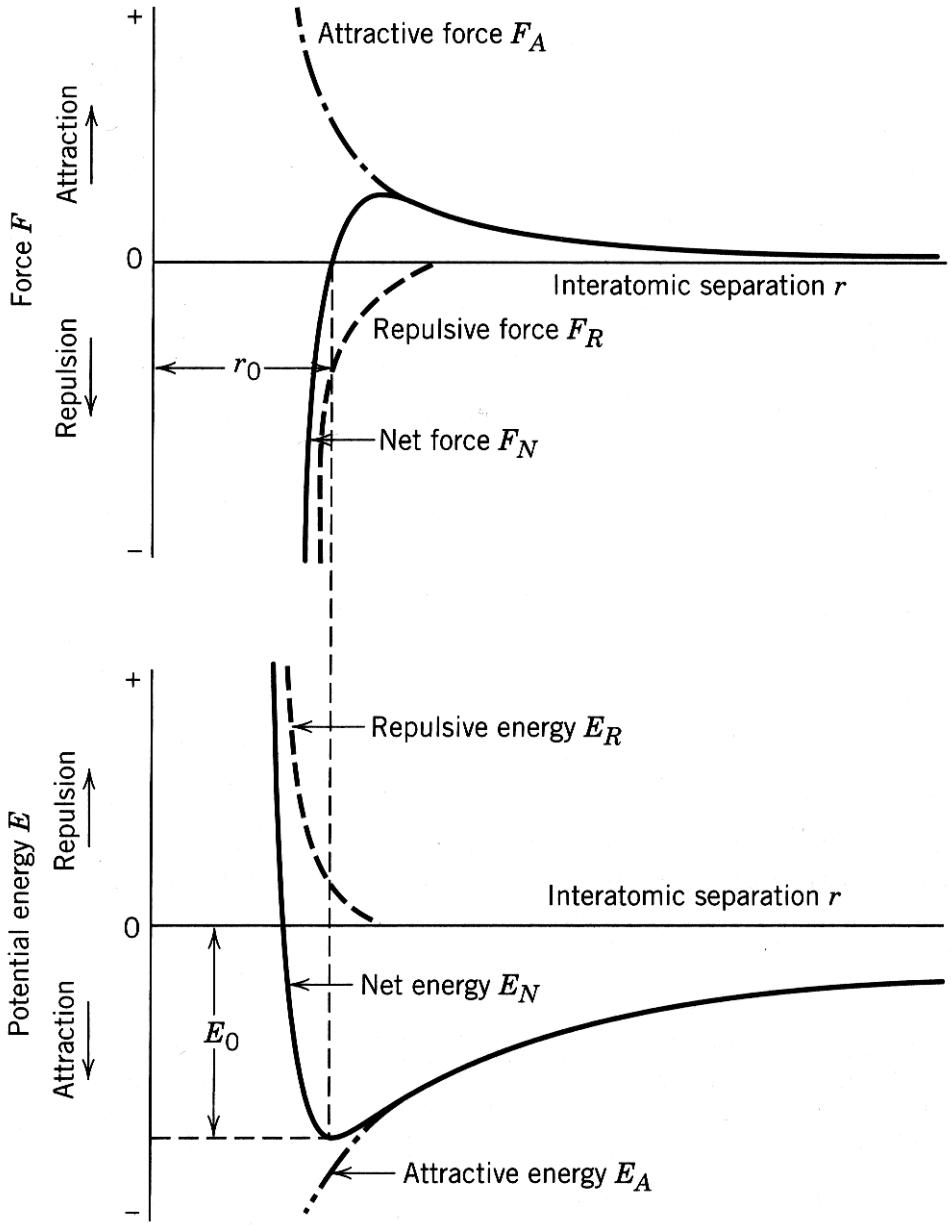
Electronegativities of C and H are similar so electrons are shared in sp^3 hybrid covalent bonds.



From J. E. Brady and F. Senese, *Chemistry: Matter and Its Changes*, 4th edition, 2004. Reprinted with permission of John Wiley & Sons, Inc



Bonding Forces & Energies



$$F_N = F_A + F_R = 0$$

$$E_N = E_A + E_R \quad F = dE/dr$$

- Covalent bonding

F_A **: nucleus to electrons**

F_R **: nucleus to nucleus**

: electrons to electrons

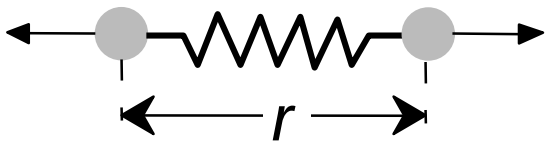
- Ionic bonding

F_A **: electrostatic attraction between unlike ions**

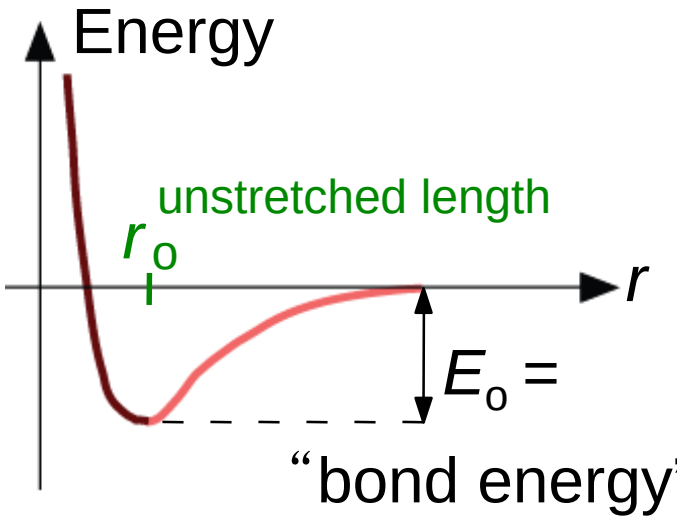
F_R **: closed shell overlapping**

(a) Properties From Bonding: T_m

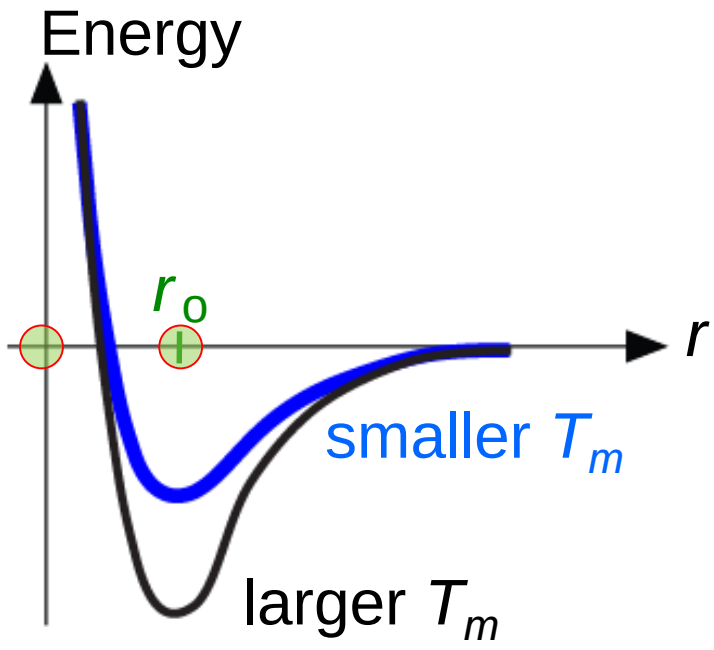
- Bond length, r



- Bond energy, E_o



- Melting Temperature, T_m

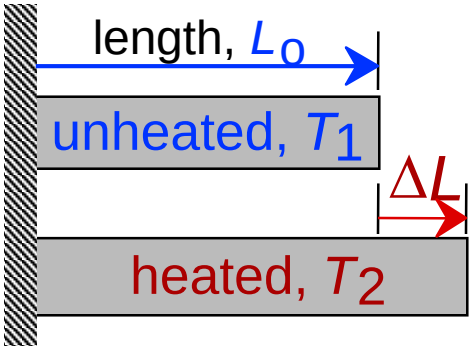


T_m is larger if E_o is larger.

두원자를 무한대로 분리시키기 위해 필요한 에너지

Properties From Bonding : α

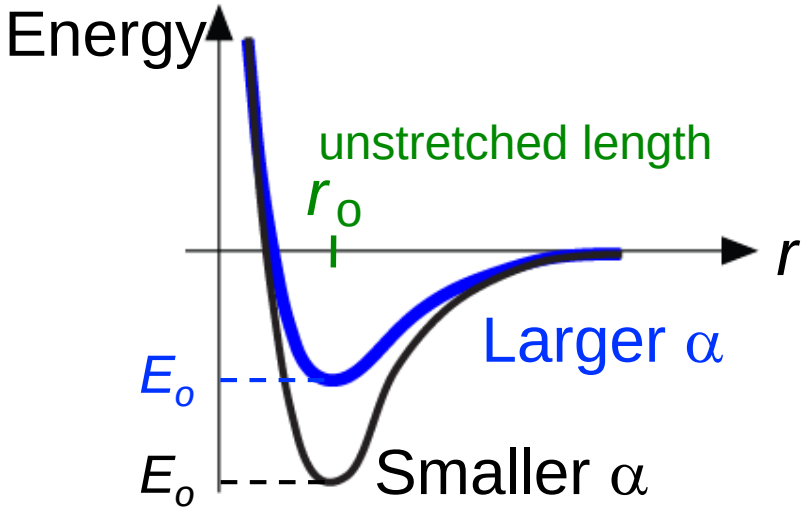
- Coefficient of thermal expansion, α



coeff. thermal expansion

$$\frac{\Delta L}{L_o} = \alpha\,(T_2 - T_1)$$

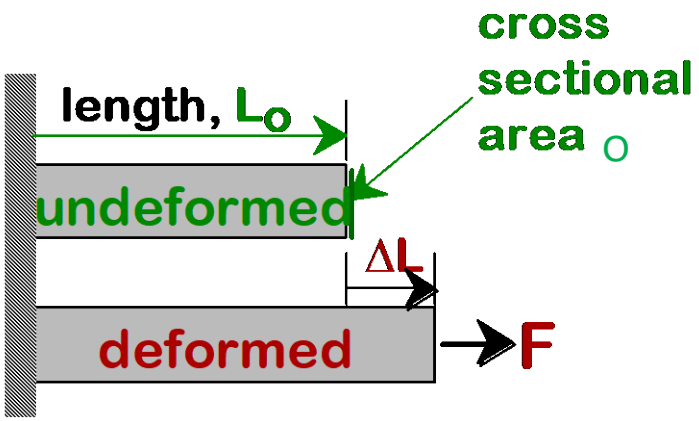
- α ~ symmetry at r_o



α is larger if E_o is smaller.

(c) Properties from Bonding: E

- **Elastic (Young's) modulus, E (y)**



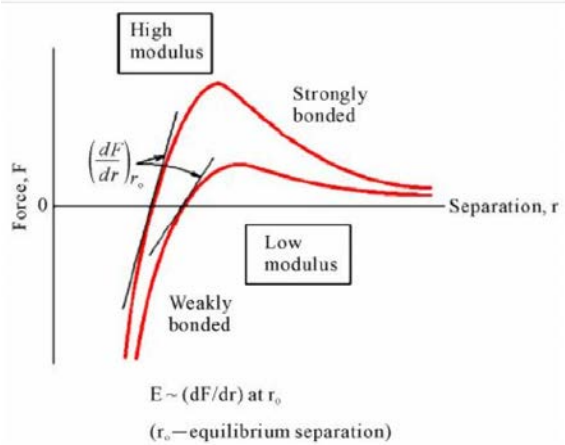
Elastic modulus

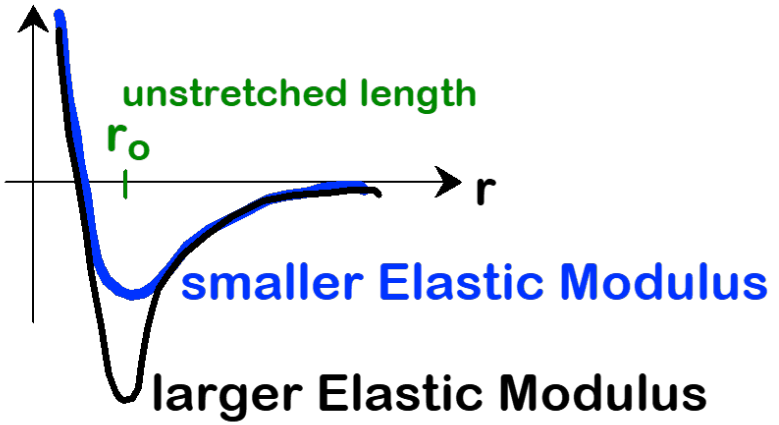
$$\frac{F}{A_o} = E\frac{\Delta L}{L_o}$$

$$\sigma = E\varepsilon$$

- E ~ curvature at r_o (the bottom of the well)

$$Y \sim \left(\frac{d^2E}{dr^2}\right)_{r_o}$$

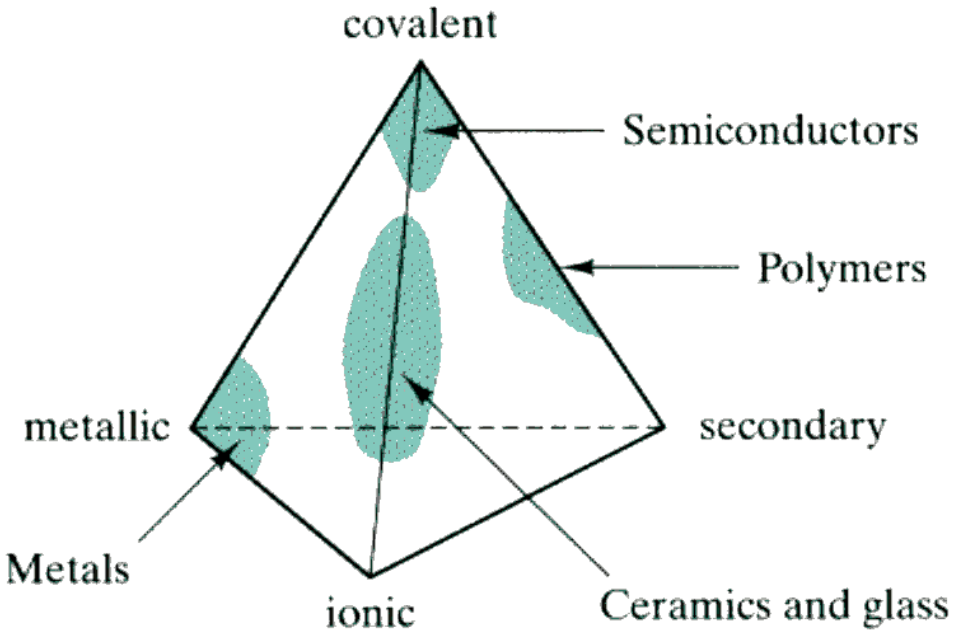




E is larger if E_o is larger

Materials-Bonding Classification

Material type	Bonding character	Example
Metal	Metallic	Iron (Fe) and the ferrous alloys
Ceramics and glasses	Ionic/covalent	Silica (SiO_2): crystalline and noncrystalline
Polymers	Covalent and secondary	Polyethylene $+C_2H_4+_n$
Semiconductors	Covalent or covalent/ionic	Silicon (Si) or cadmium sulfide (CdS)



< 실제 많은 재료는 2개 혹은 그 이상의 결합에 혼합 >

Summary: Properties from Bonds

Ceramics

(Ionic & covalent bonding):

Large bond energy

large T_m
large E
small α

Metals

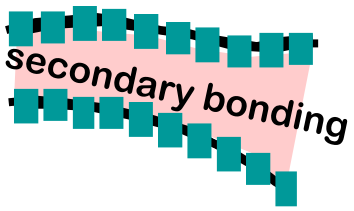
(Metallic bonding):

Variable bond energy

moderate T_m
moderate E
moderate α

Polymers

(Covalent & Secondary):

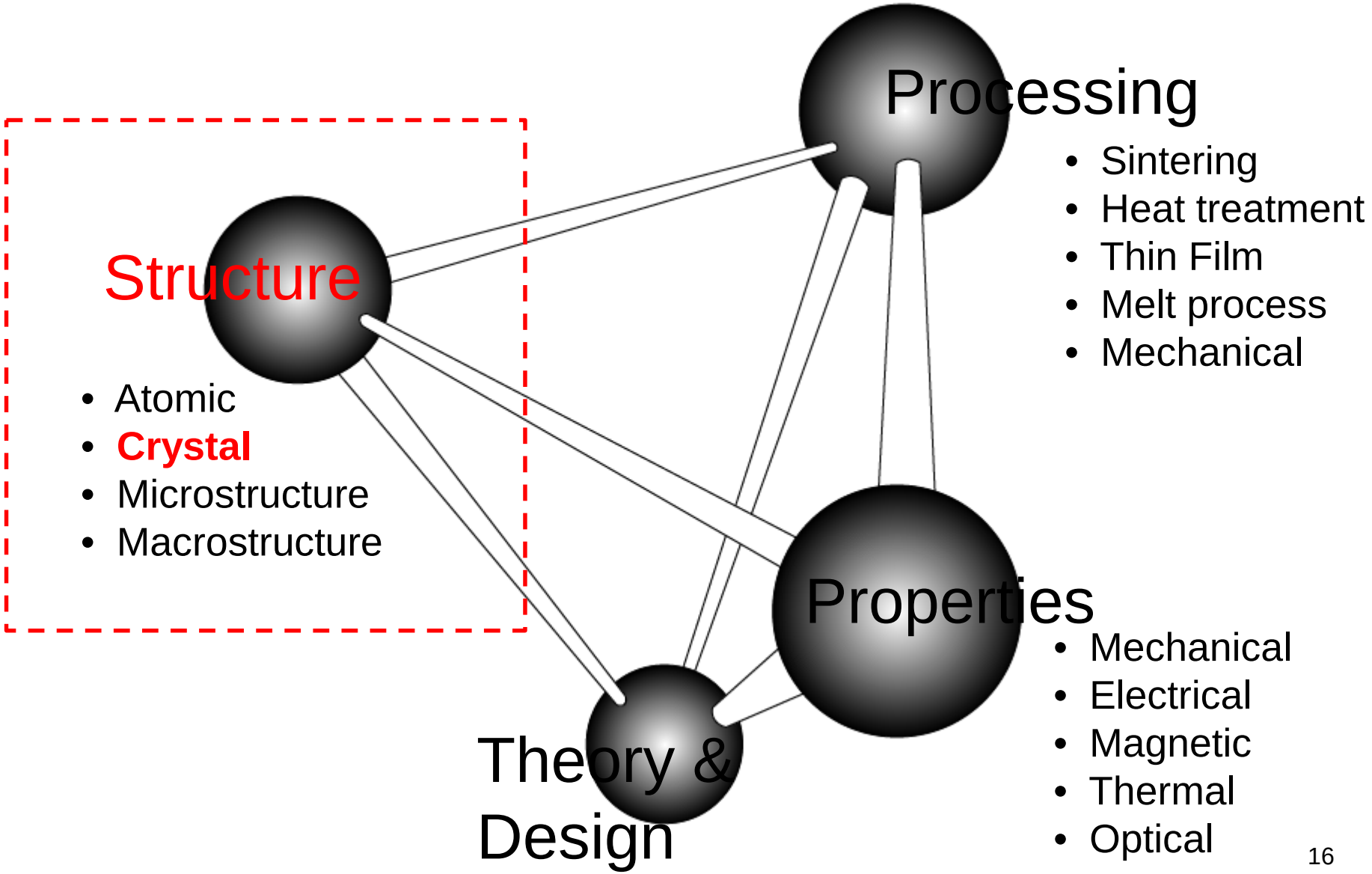


Directional Properties

Secondary bonding dominates

small T_m
small E
large α

Materials Science and Engineering



- Sintering
- Heat treatment
- Thin Film
- Melt process
- Mechanical

- Atomic
- **Crystal**
- Microstructure
- Macrostructure

- Mechanical
- Electrical
- Magnetic
- Thermal
- Optical

Contents for today's class

CHAPTER 3: Fundamentals of Crystallography

I. Crystal Structures

- Lattice, Unit Cells, Crystal system

II. Crystallographic Points, Directions, and Planes

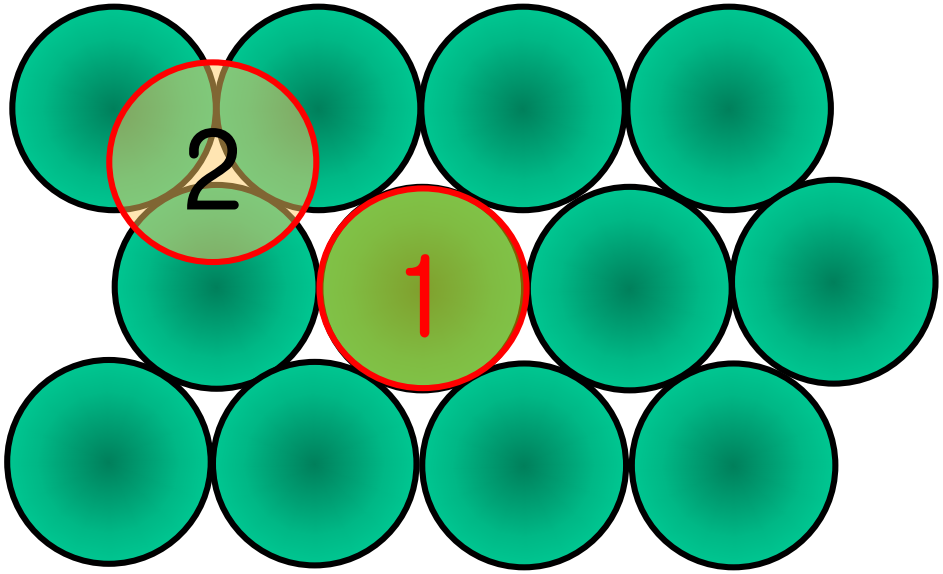
- Point coordinates, Crystallographic directions, Crystallographic planes

III. Crystalline and Noncrystalline Materials

- Single crystals, Polycrystalline materials, Anisotropy, Noncrystalline solids

Stacking of atoms in solid

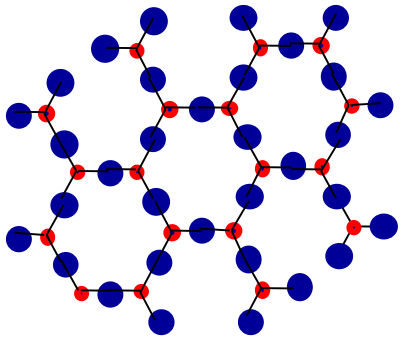
Finding stable position



- Minimize energy configuration
  - Related to the bonding nature

Materials and Packing

Crystalline materials...
- atoms pack in periodic, 3D arrays
- typical of: -metals
  -many ceramics
  -some polymers



crystalline SiO_2

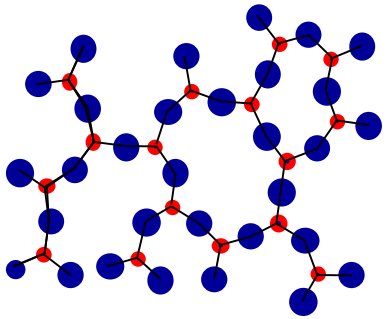
Adapted from Fig. 3.22(a), *Callister 7e.*

Quasicrystalline materials...

Noncrystalline materials...
- atoms have no periodic packing
- occurs for: -complex structures
  -rapid cooling

"Amorphous" = Noncrystalline

• Si ● Oxygen



noncrystalline SiO_2

atomic arrangement in the solid state

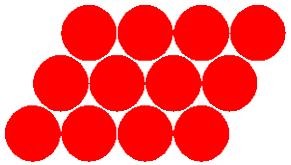
- Solid materials are classified according to the **regularity** with which atoms and ions are arranged with respect to one another.

- So, how are they arranged ?

  (a) **periodically** – having long range order in 3-D

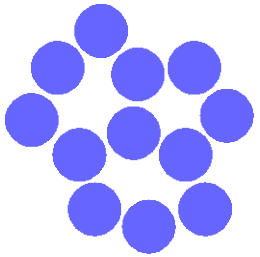
  (b) **quasi-periodically**

  (c) **randomly** – having short range order with the characteristics of bonding type but losing the long range order



Crystal

Quasicrystal



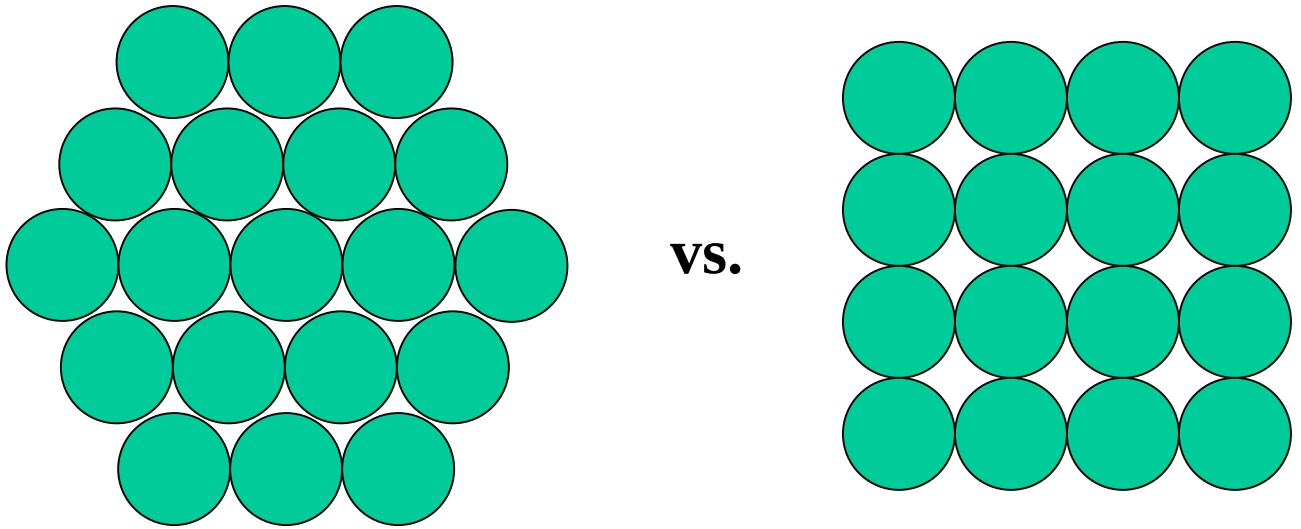
Amorphous

- **Crystal: Perfection → Imperfection**

I. Crystal structures

- **How can we stack metal atoms to minimize empty space?**

2-dimensions



Now stack these 2-D layers to make 3-D structures

Crystalline materials - three-dimensional periodic arrangement of atoms, ions, or molecules- translational periodicity

Crystal – related topics

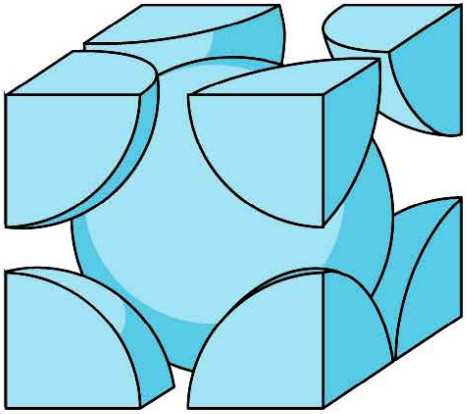
- Periodicity (주기성)
- Symmetry (대칭성)
- Anisotropy (비등방성)
- Directions and Planes (방향과 면)
- Interplanar spacing & angles (면간거리와 각도)
- Diffraction (회절)

I. Crystal structure

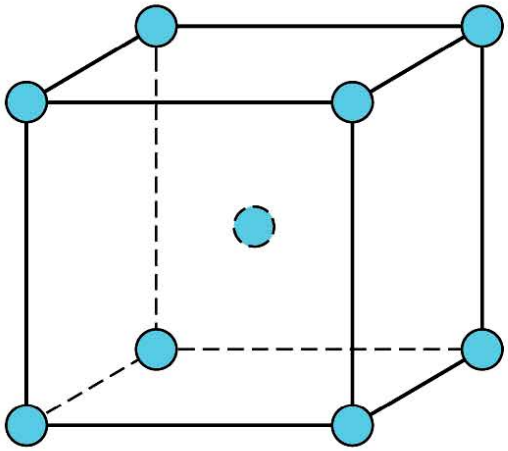
(1) Lattice : 결정 공간상에서 점들의 규칙적인 기하학적 배열

- 3D point array in space, such that each point has identical surroundings. These points may or may not coincide with atom positions.
- Simplest case : each atom → its center of gravity → point or space lattice → pure mathematical concept

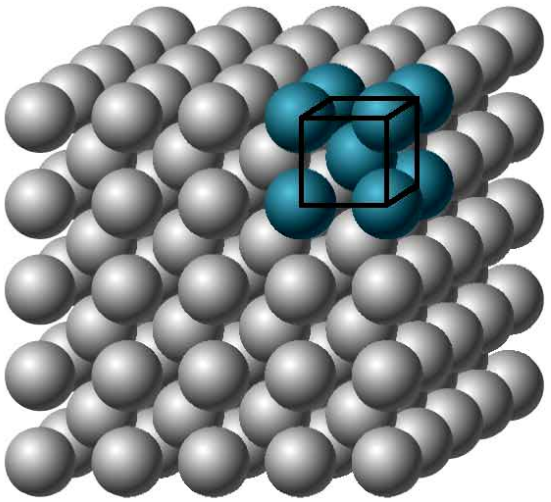
example: sodium (Na) ; body centered cubic



Hard-sphere unit cell



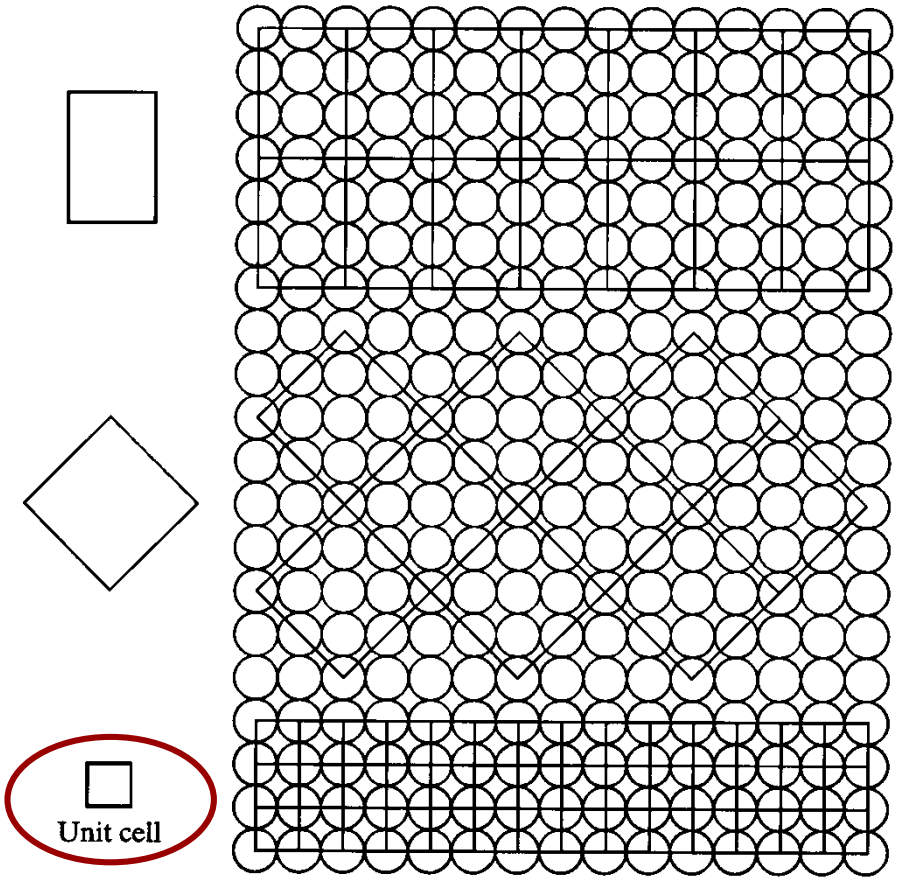
Reduced sphere unit cell



Aggregate of many atoms

(2) Unit cell

: smallest repetitive volume which contains the complete lattice pattern of a crystal



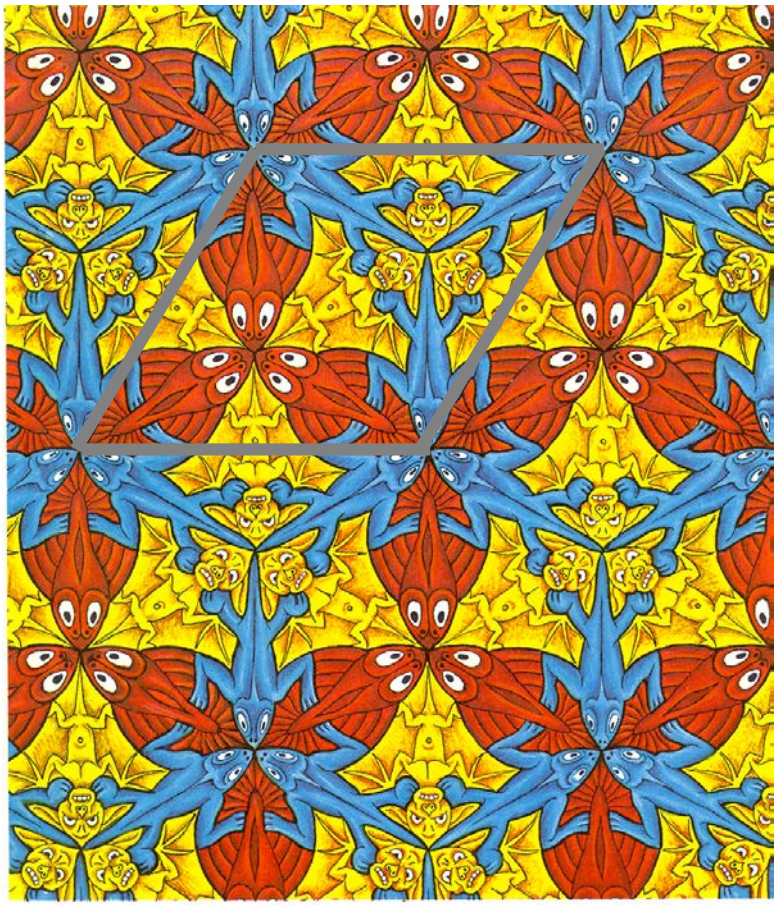
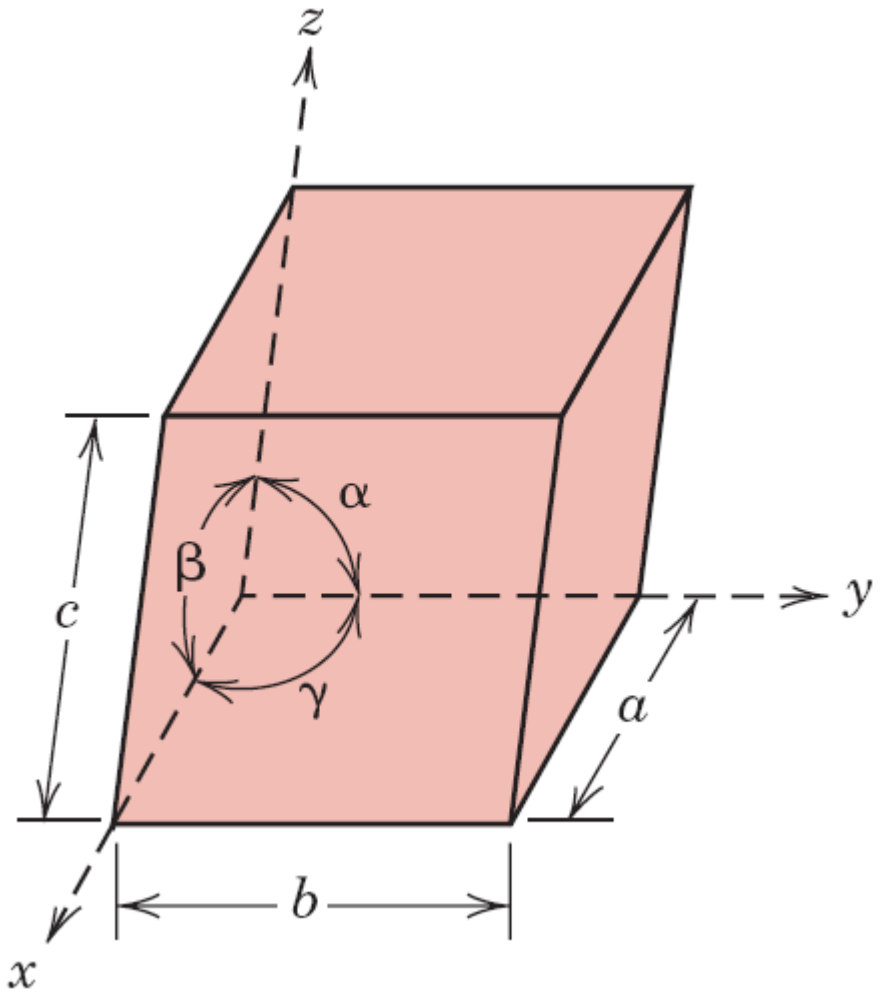


PLATE 9

Unit cell

(3) Lattice parameter

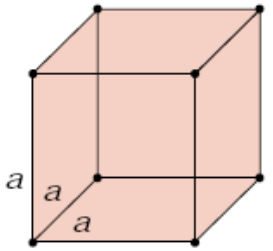
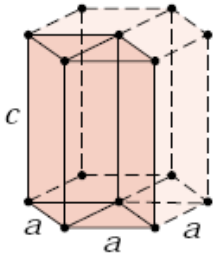
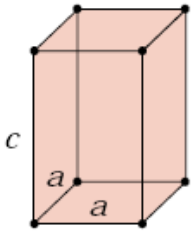


length: a, b, c

angle: α, β, γ

(4) 7 crystal systems

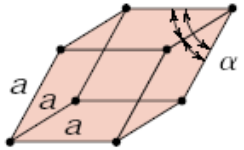
Unit cell

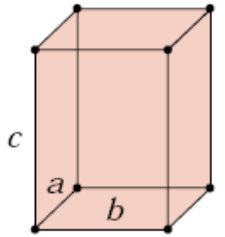
Crystal System	*Axial Relationships*	*Interaxial Angles*	*Unit Cell Geometry*
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	

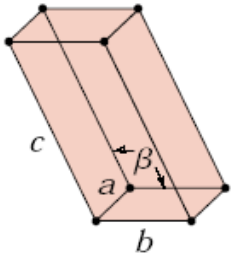
(4) 7 crystal systems (continued)

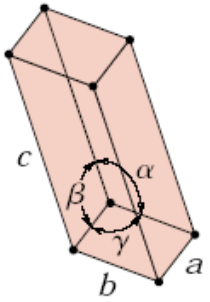
Unit cell

Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90° \neq \beta$
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$





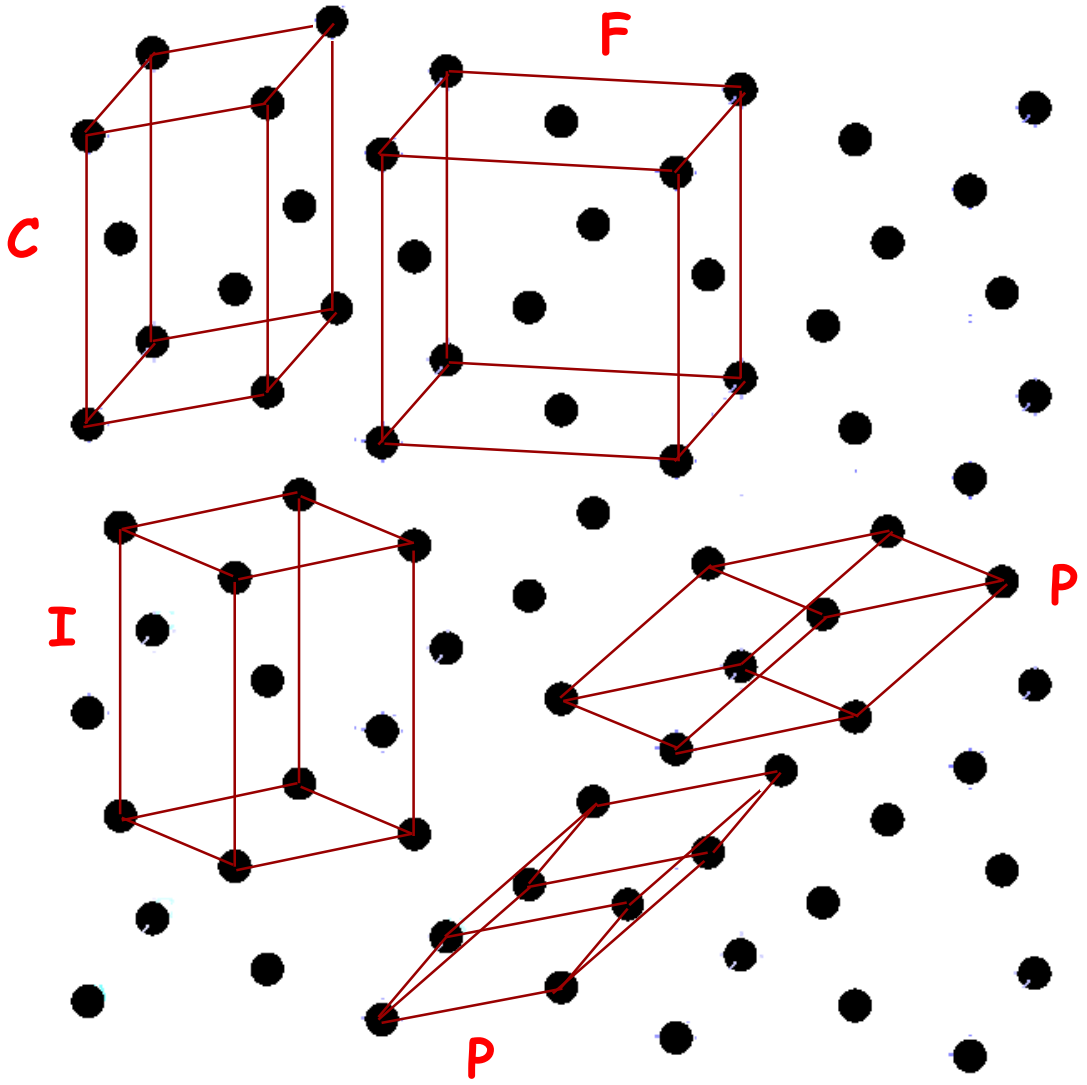




Unit cell

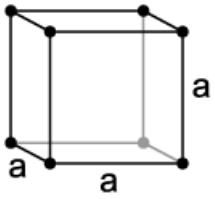
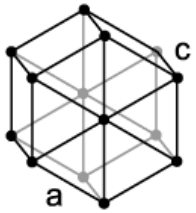
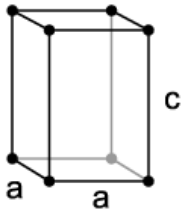
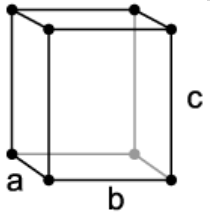
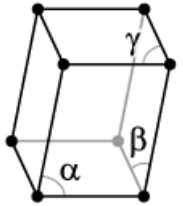
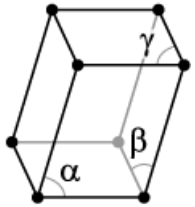
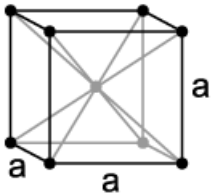
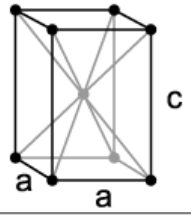
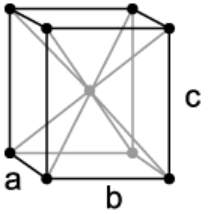
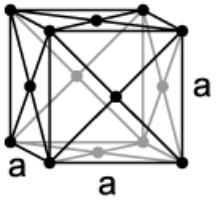
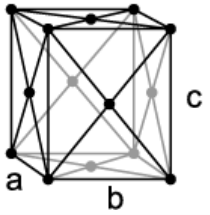
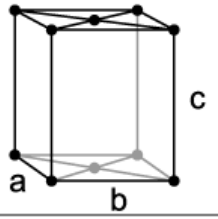
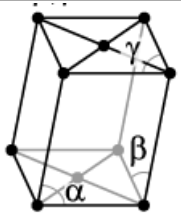
- **P, I, F, C**

- ❑ ***P*** **: Primitive**
- ❑ ***I*** **: Body centered**
- ❑ ***F*** **: Face centered**
- ❑ ***C*** **: Base centered**



Unit cell

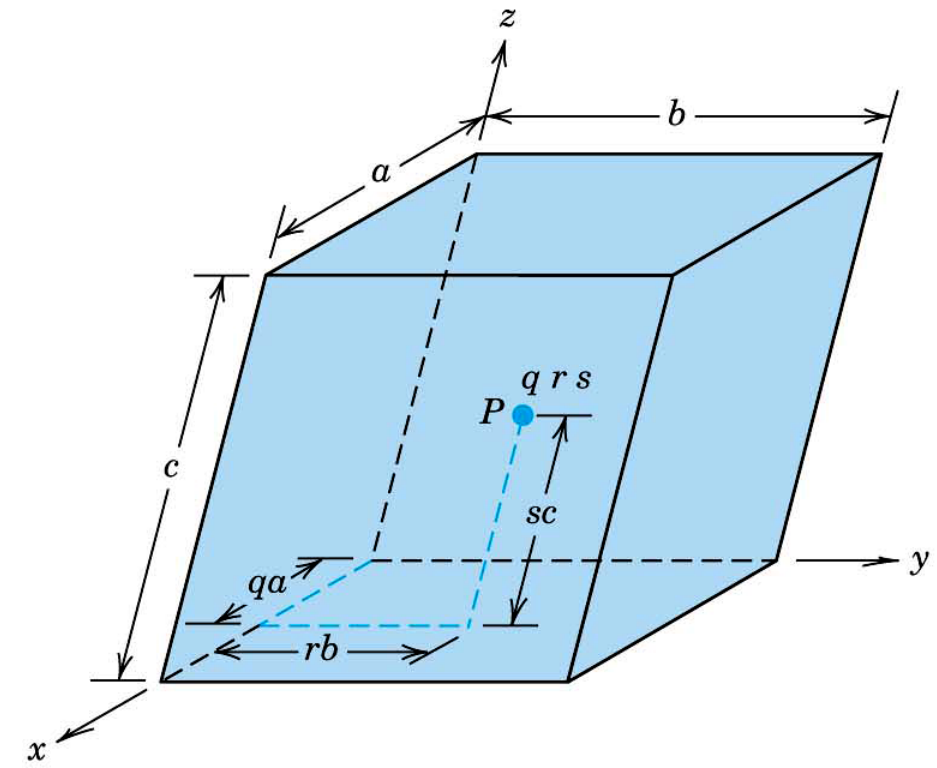
(5) 14 Bravais Lattice - Only 14 different types of unit cells are required to describe all lattices using symmetry

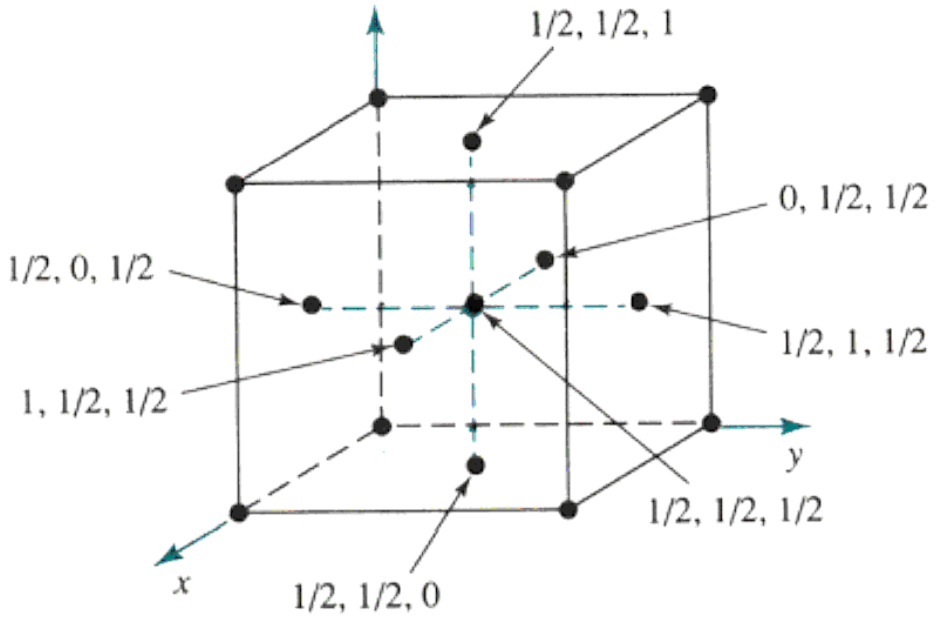
	cubic	hexagonal	rhombohedral (trigonal)	tetragonal	orthorhombic	monoclinic	triclinic
P							
I							
F							
C							

II. Crystallographic points, directions and planes

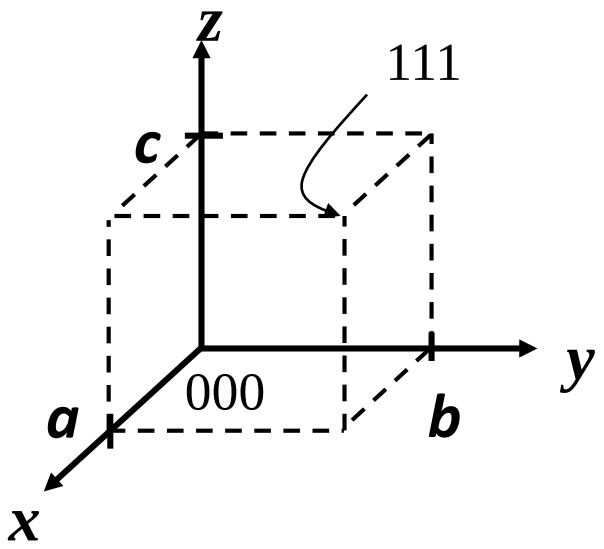
Chapter 3.5 Point coordinates

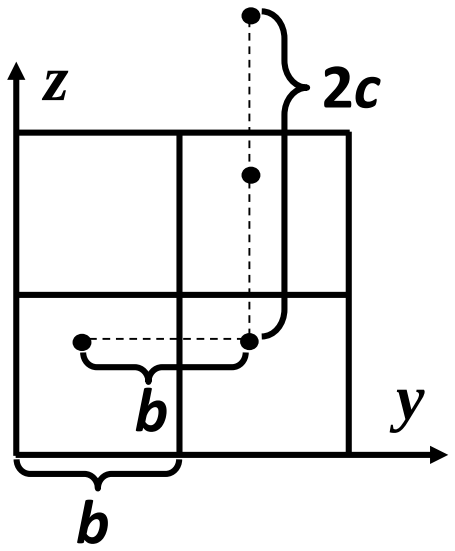
- **position: fractional multiples of the unit cell edge lengths**
  - **ex) P: q,r,s**





cubic unit cell





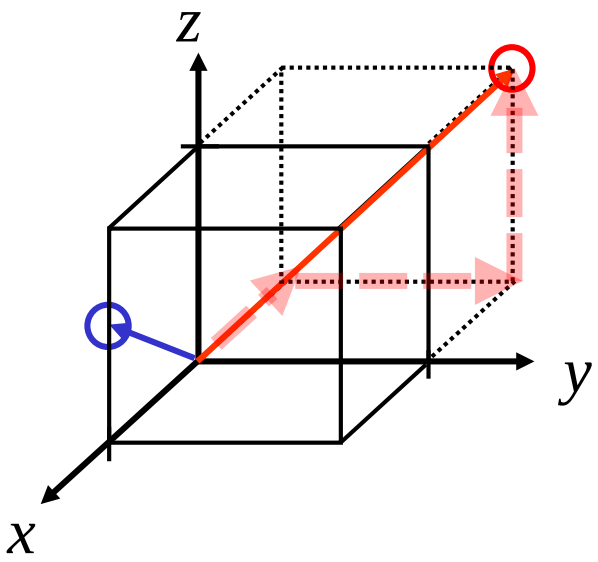
Point coordinates for unit cell center are

***a*/2, *b*/2, *c*/2** ½ ½ ½

Point coordinates for unit cell corner are 111

Translation: integer multiple of lattice constants → identical position in another unit cell

Crystallographic Directions



Algorithm

1. Vector repositioned (if necessary) to pass through origin.
2. Read off projections in terms of unit cell dimensions *a*, *b*, and *c*
3. Adjust to smallest integer values
4. Enclose in square brackets, no commas

[*uvw*]

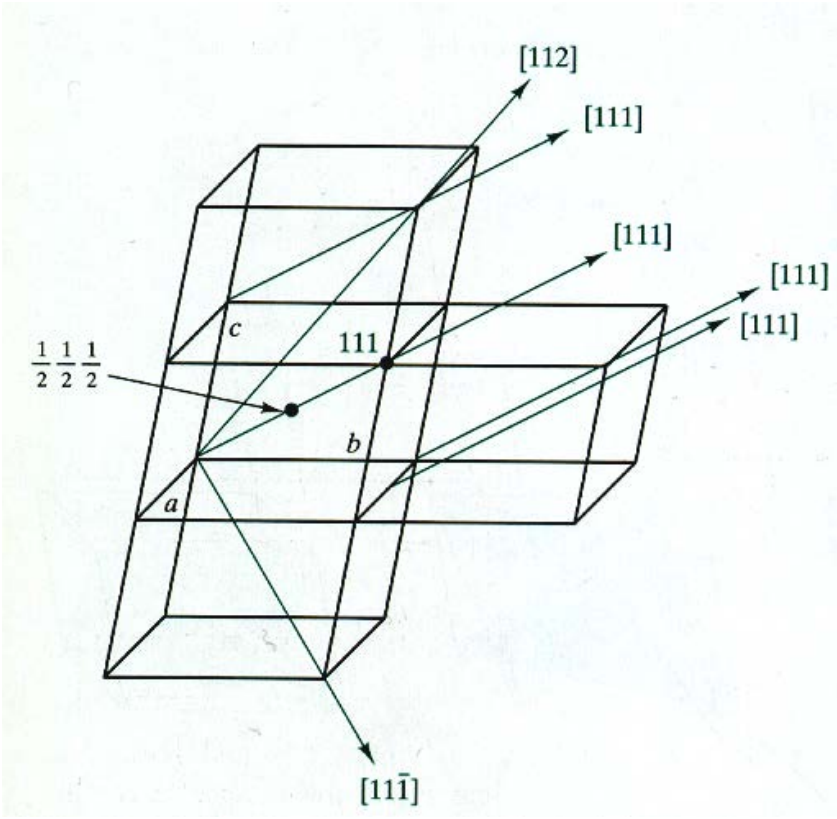
ex: 1, 0, ½ => 2, 0, 1 => [201]

-1, 1, 1 => $[\bar{1}11]$ where overbar represents a negative index

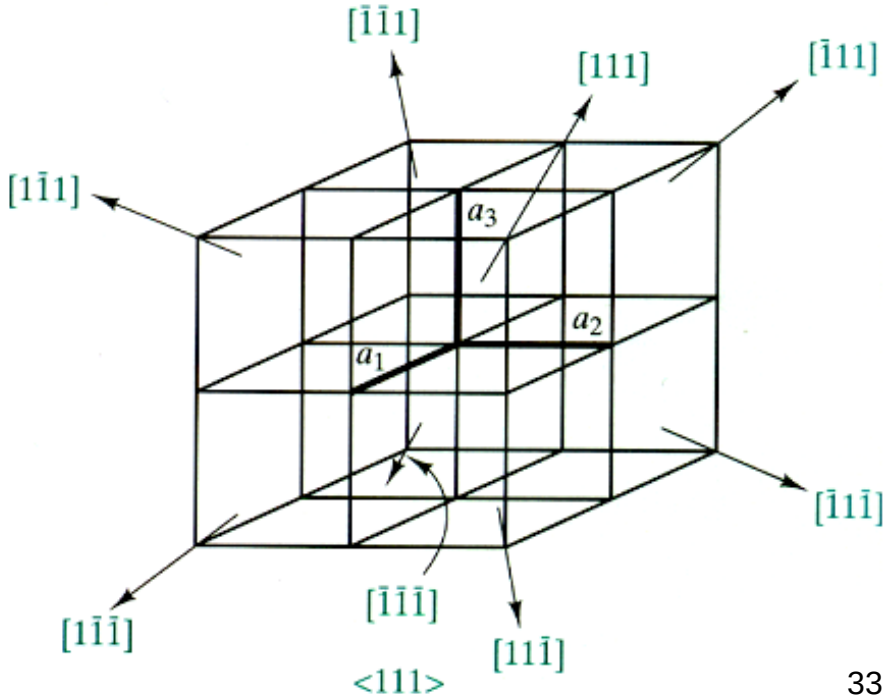
families of directions <*uvw*>

Crystallographic Directions

- a line between two points or a vector
- [uvw] square bracket, <u>smallest integer</u>
- families of directions: <uvw> angle bracket



cubic



Directional indices

<100> ⇒ [100], [010], [001]
[$\bar{1}$00], [0$\bar{1}$0], [00$\bar{1}$]

<110> ⇒ [110], [101], [011],
[$\bar{1}\bar{1}$0], [$\bar{1}$0$\bar{1}$], [0$\bar{1}\bar{1}$],
[1$\bar{1}$0], [10$\bar{1}$], [01$\bar{1}$],
[$\bar{1}$10], [$\bar{1}$01], [0$\bar{1}$1]

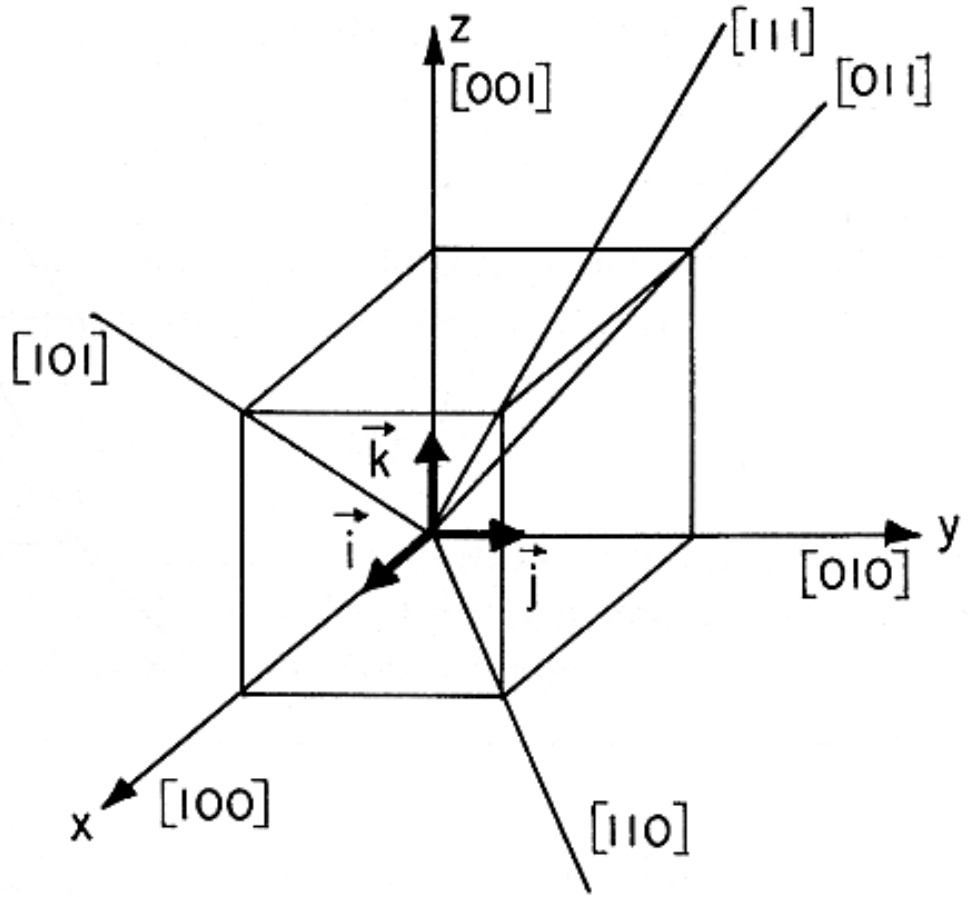
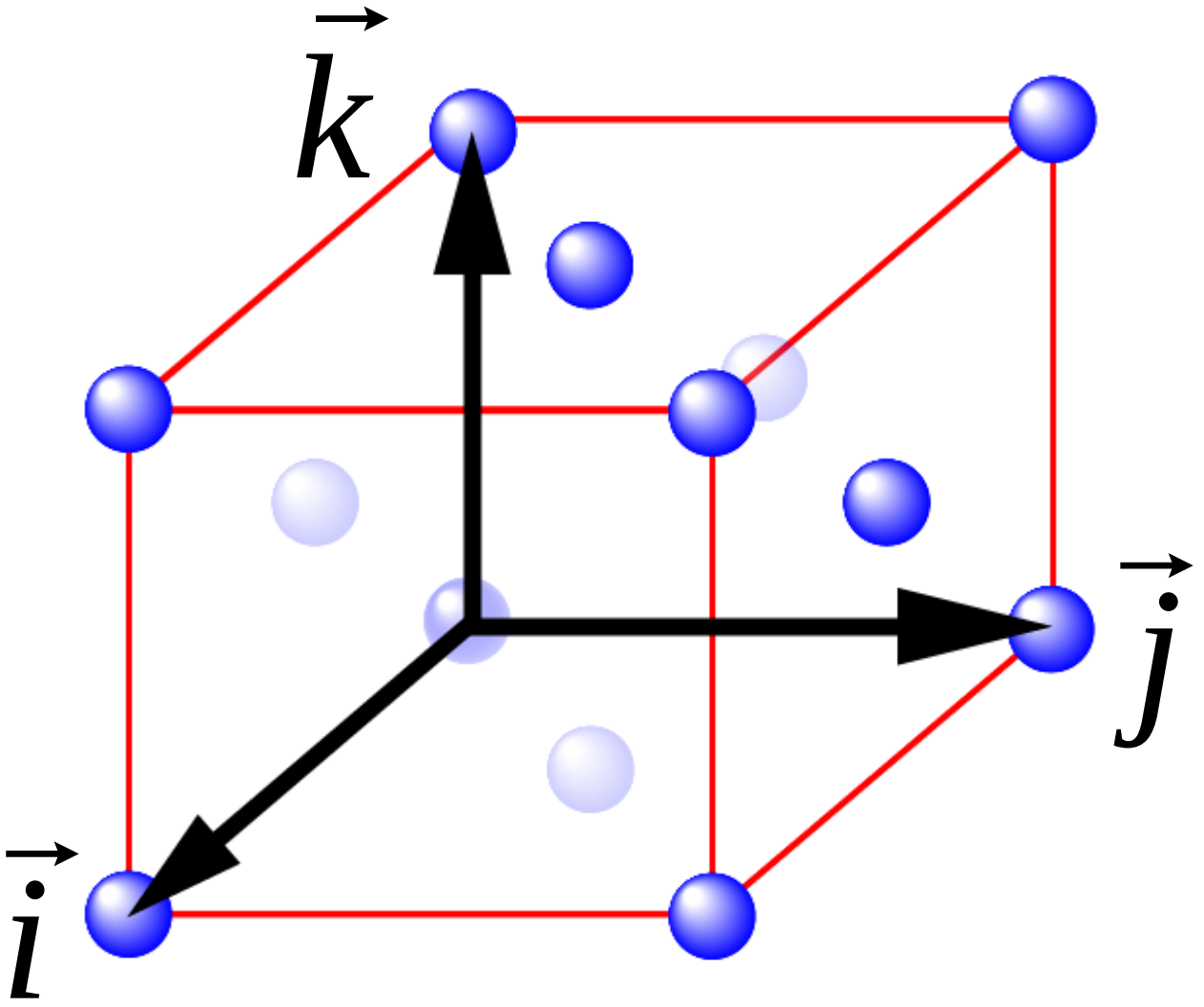


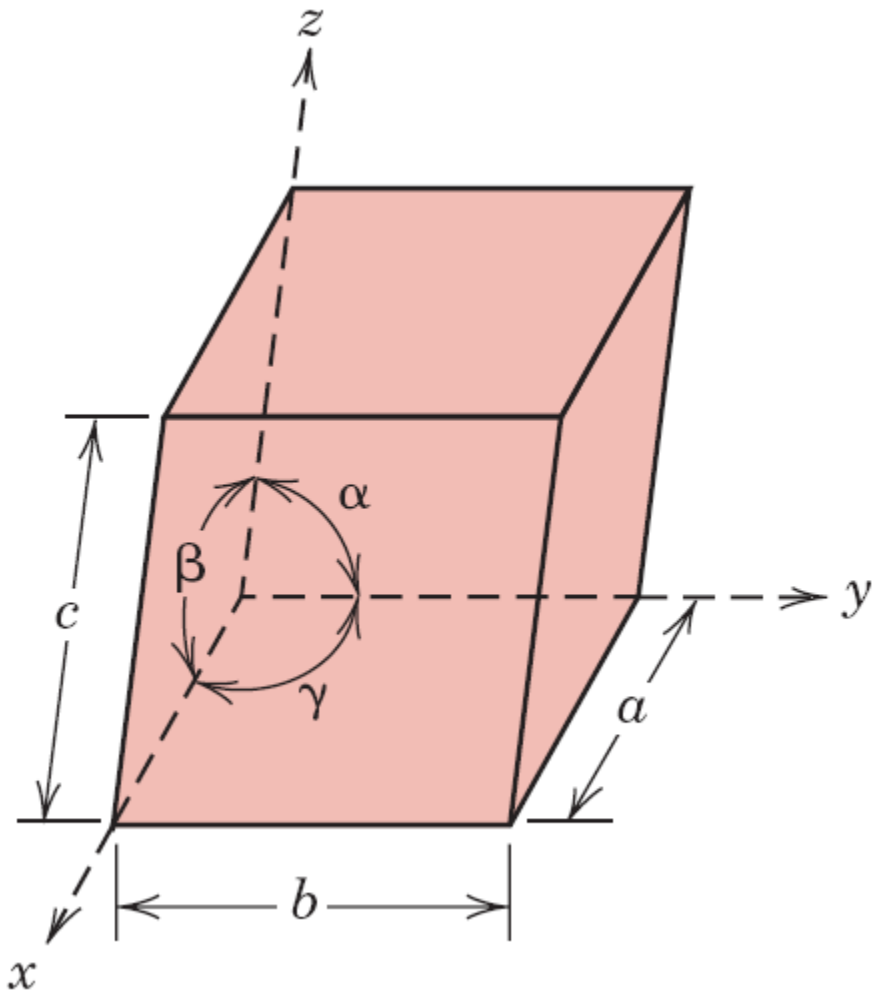
Figure 1.8 Directions in a cubic unit cell.

< *i j k* > : permutation of [*i j k*]

Impose index coordination



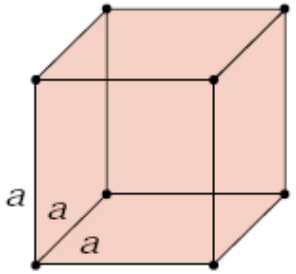
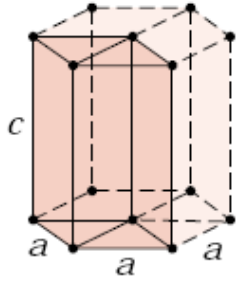
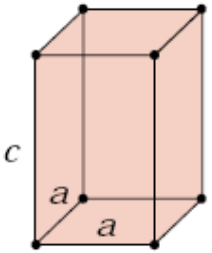
Lattice Parameter



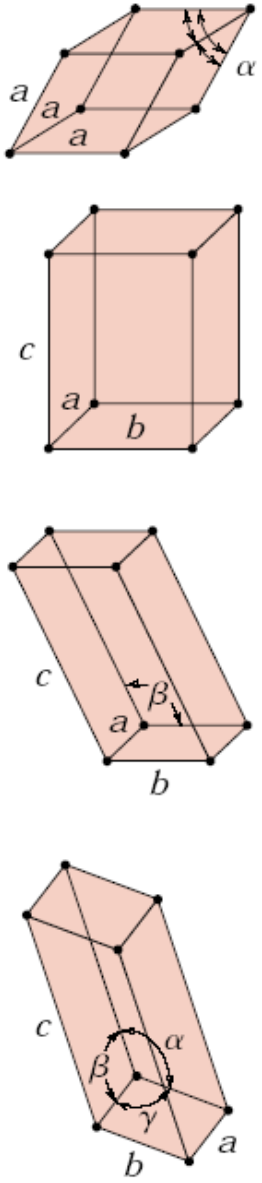
length: a, b, c

angle: α, β, γ

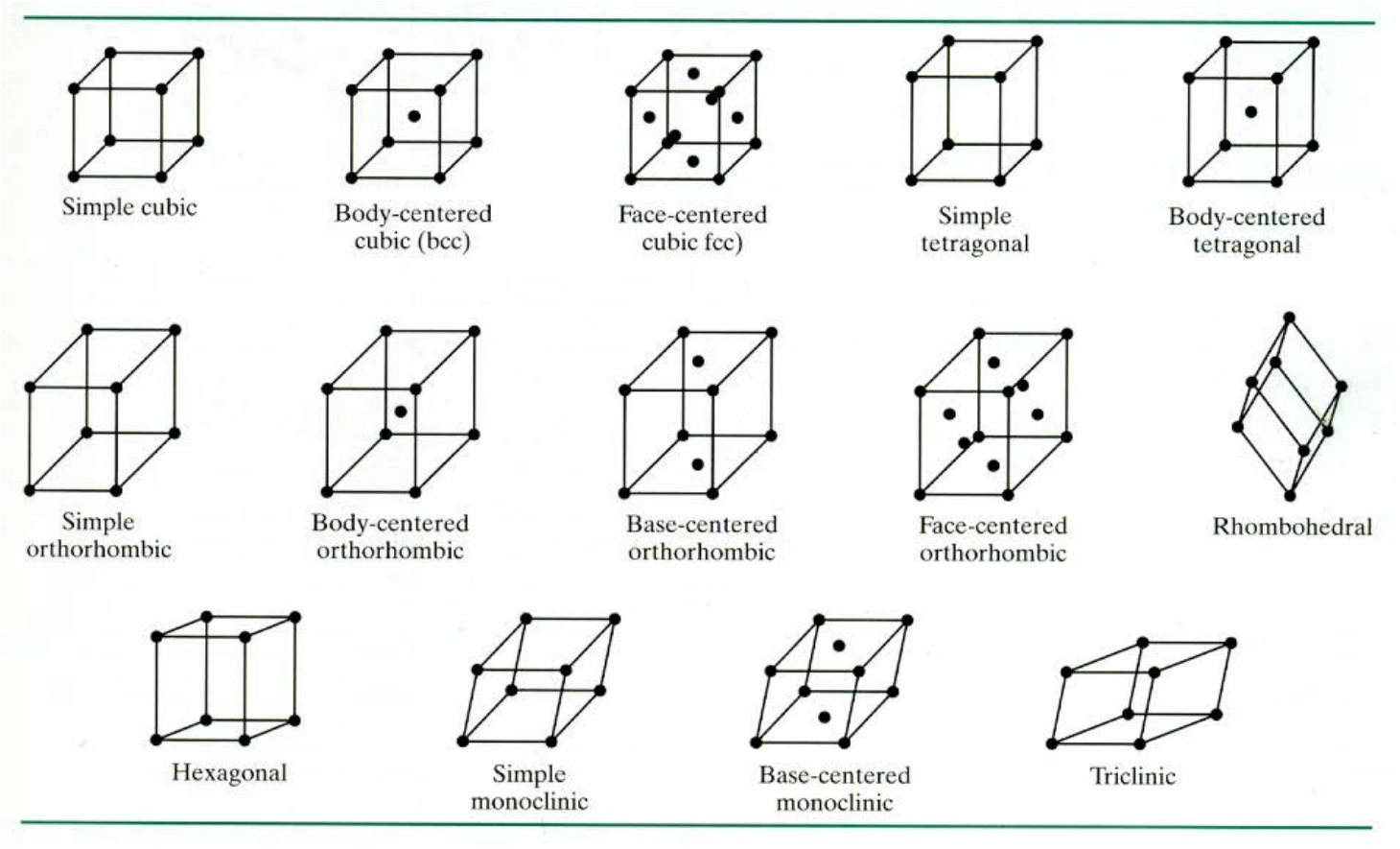
Table 3.6 Lattice Parameter Relationships and Figures Showing Unit Cell Geometries for the Seven Crystal Systems

Crystal System	*Axial Relationships*	*Interaxial Angles*	*Unit Cell Geometry*
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	

Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90° \neq \beta$
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$

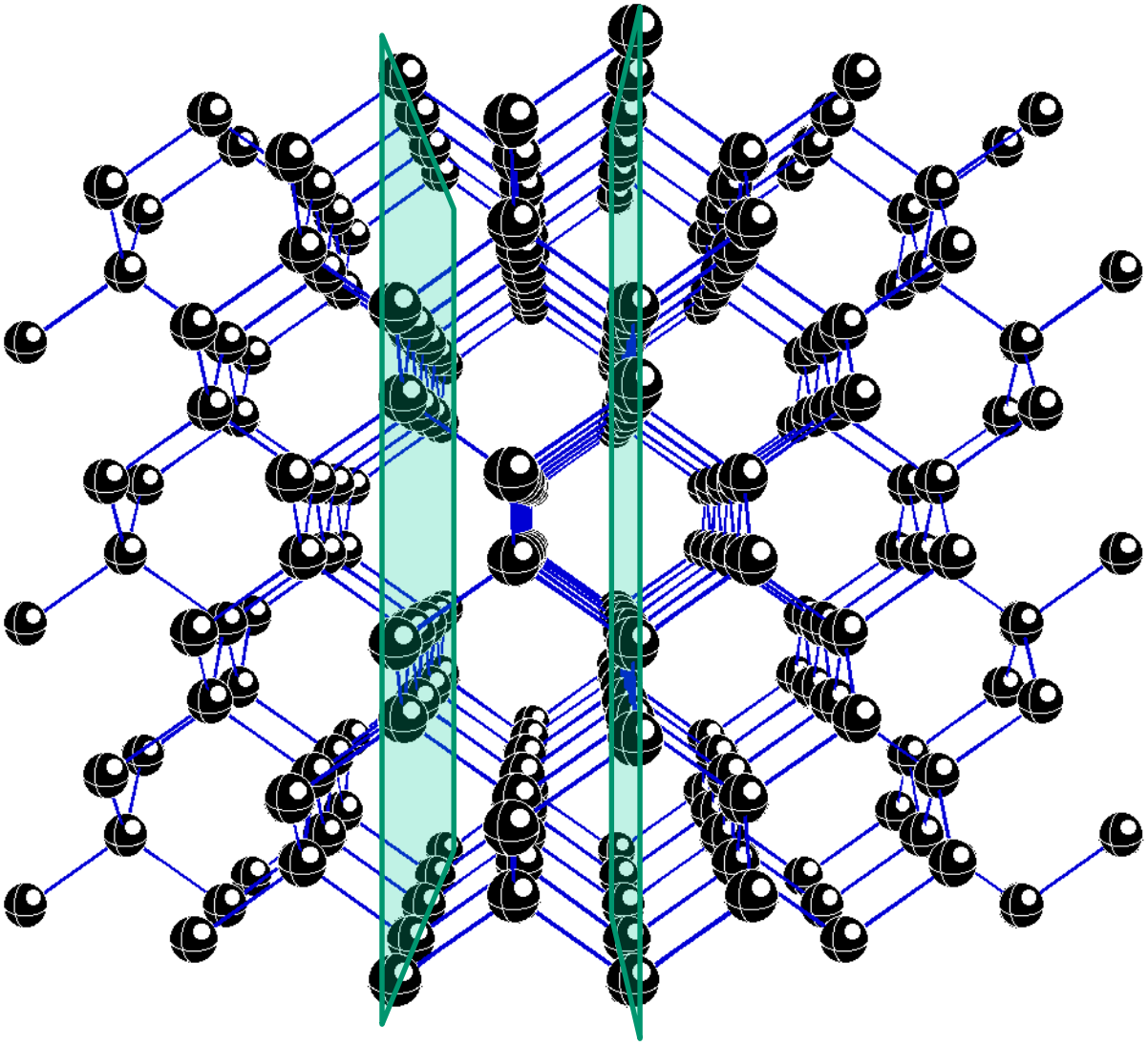


14 Bravais Lattice

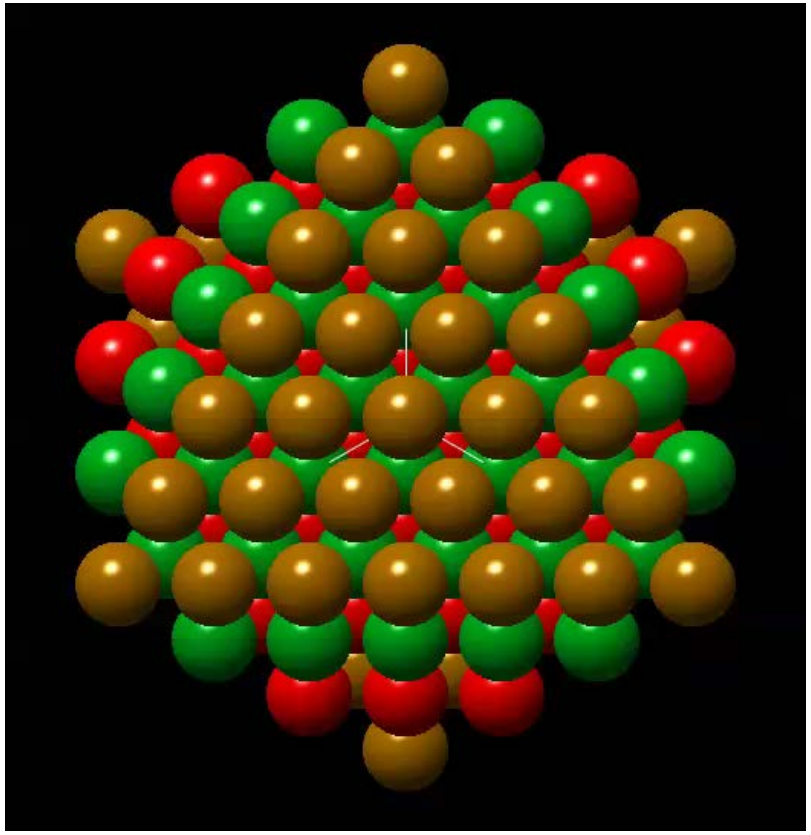


- **Only 14 different types of unit cells are required to describe all lattices using symmetry**
- **simple (1), body-centered (2), base-centered (2) face-centered (4 atoms/unit cell)**

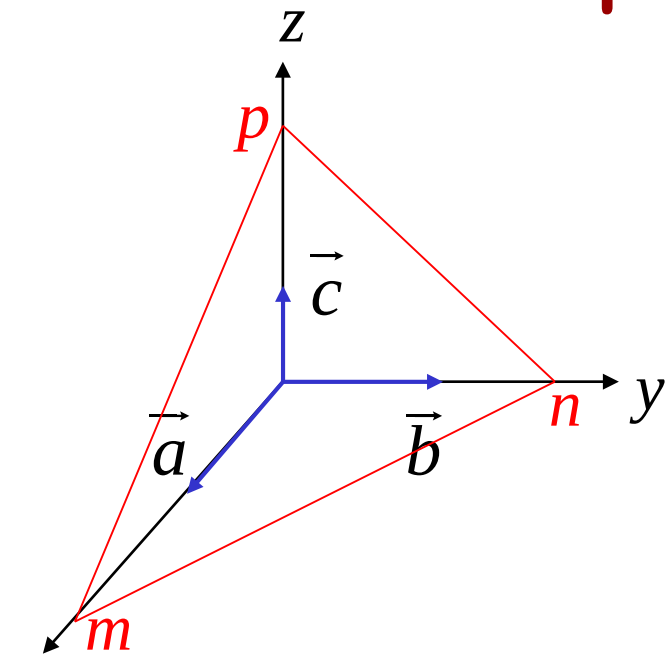
Crystal view -Silicon



Crystallographic planes



Lattice plane (Miller indices)



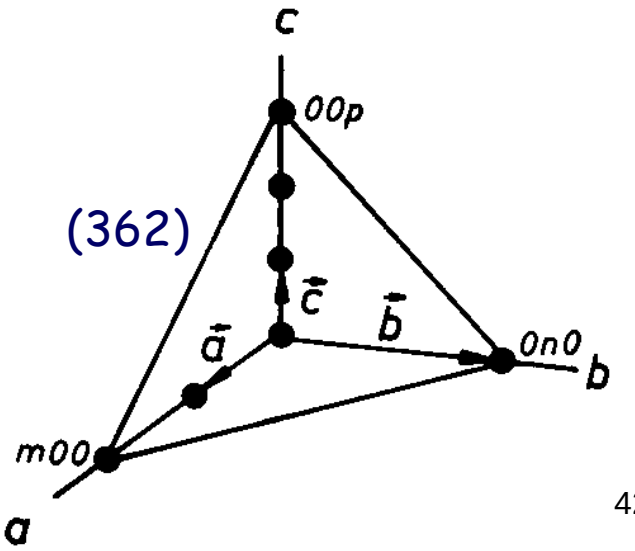
Plane (hkl)
Family of planes {hkl}

m00, 0n0, 00p: define lattice plane

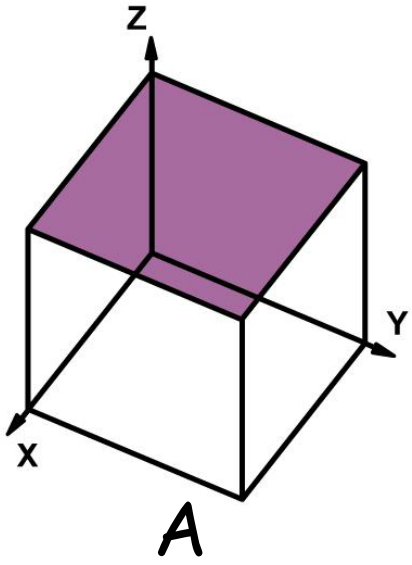
m, n, ∞ : no intercepts with axes

Intercepts @ (mnp)	2	1	3
Reciprocals	½	1	1/3
Miller indicies	3	6	2
(362) plane			

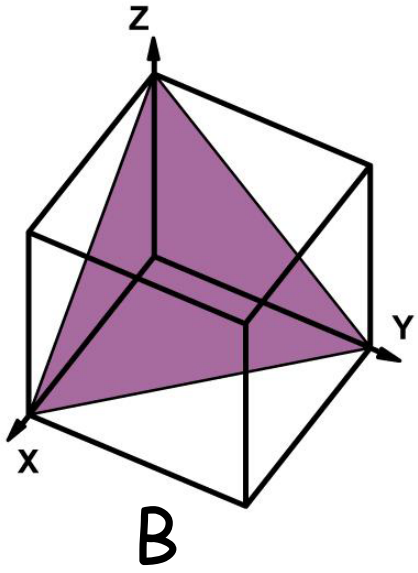
Miller indicies ; defined as the smallest integral multiples of the reciprocals of the plane intercepts on the axes



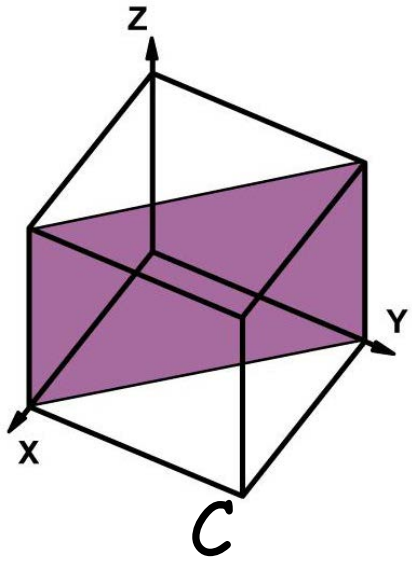
Crystallographic Planes



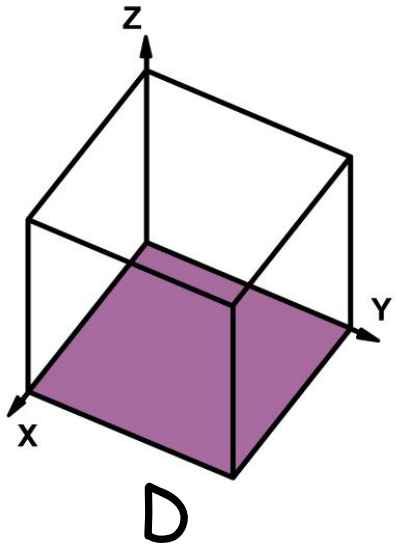
A



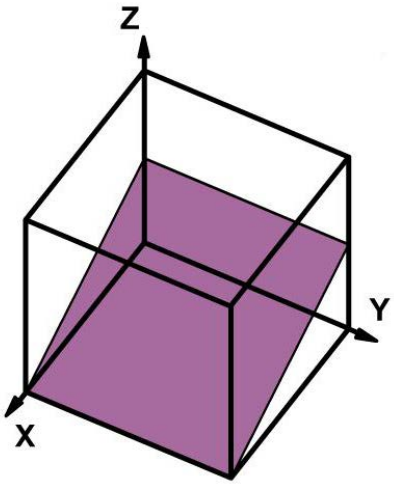
B



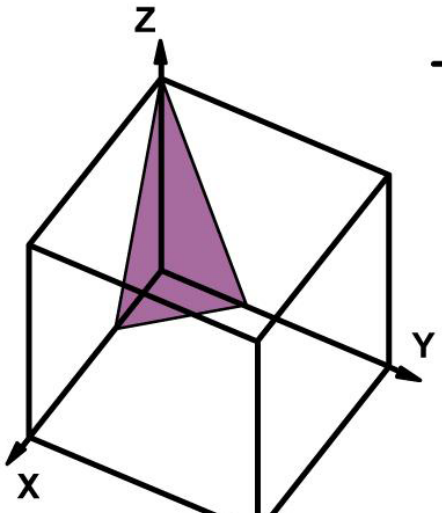
C



D



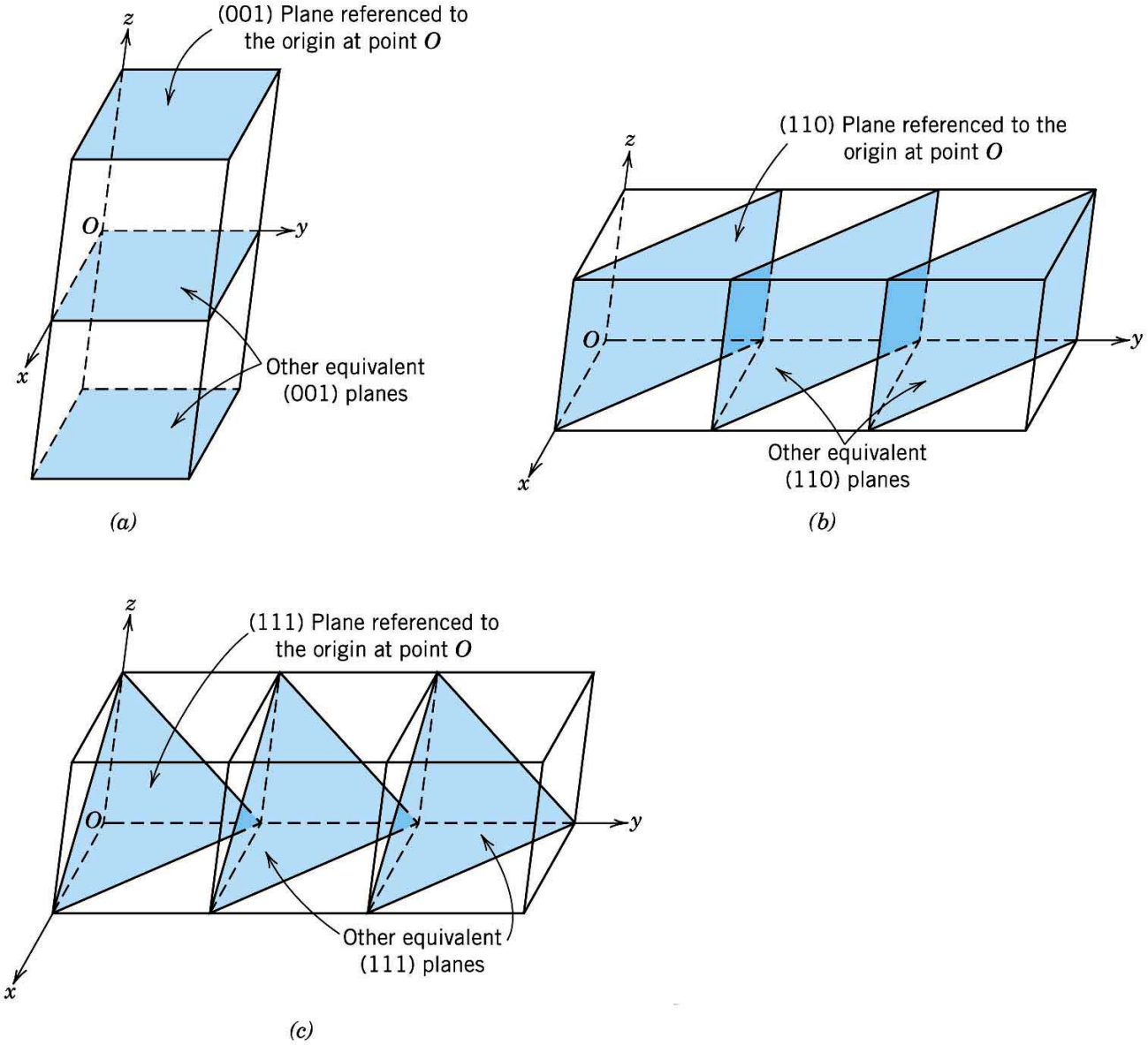
E



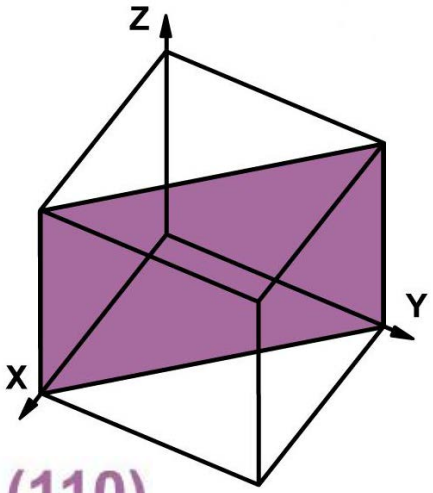
F

Plane	Intercepts	Indices
A	∞, ∞, 1	(001)
B	1, 1, 1	(111)
C	1, 1, ∞	(110)
D	∞, ∞, -1	$(00\bar{1})$
E	1, ∞, 1/2	( )
F	1/3, 1/3, 1	( )

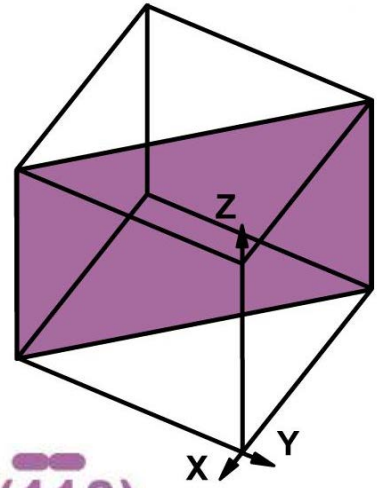
Crystallographic Planes



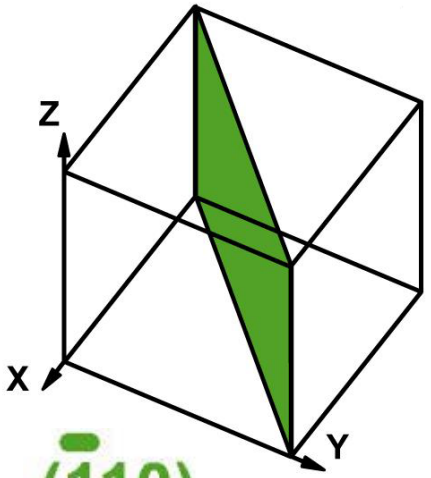
{110} Family



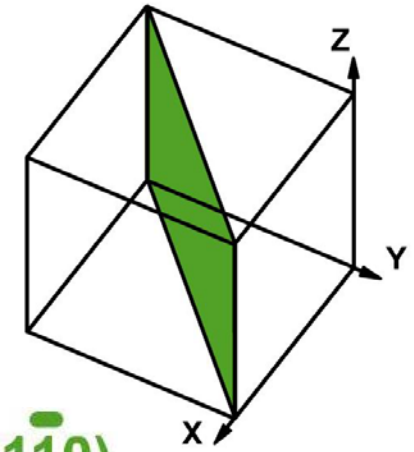
(110)



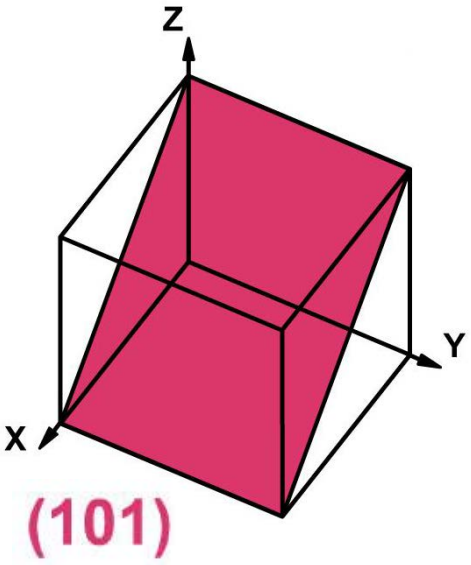
$(\bar{1}\bar{1}0)$



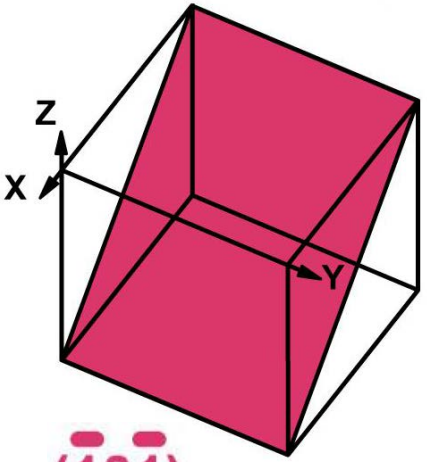
$(\bar{1}10)$



$(1\bar{1}0)$

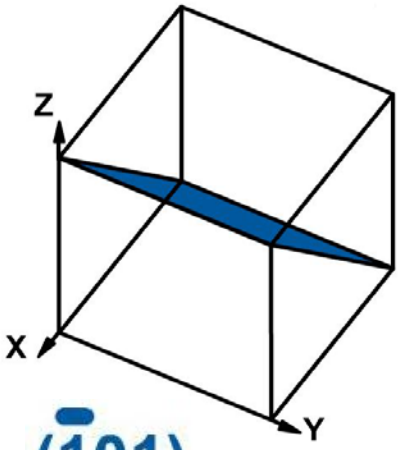


(101)

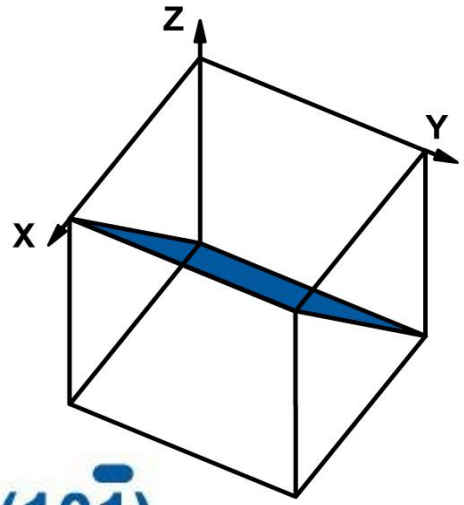


$(\bar{1}0\bar{1})$

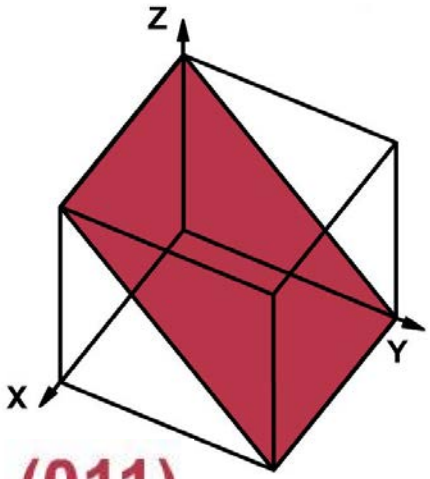
{110} Family



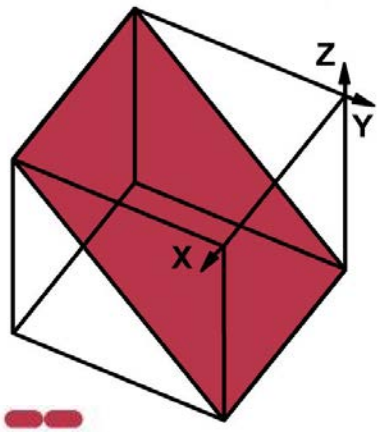
$(\bar{1}01)$



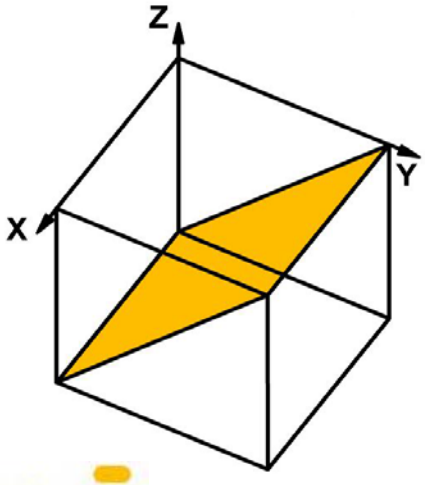
$(10\bar{1})$



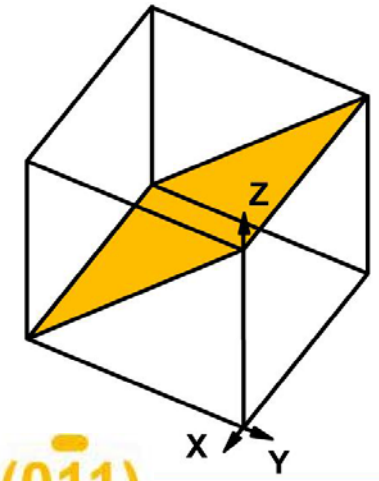
(011)



$(0\bar{1}\bar{1})$



$(01\bar{1})$



$(0\bar{1}1)$

Directions, Planes, and Family

- line, direction
  - [111] square bracket
  - <111> angular bracket - family

- Plane
  - (111) round bracket (Parentheses)
  - {111} braces - family

HCP Crystallographic Directions

- **Hexagonal Crystals**
  - **4 parameter Miller-Bravais lattice coordinates are related to the direction indices (i.e., *u′ v′ w′*) as follows.**

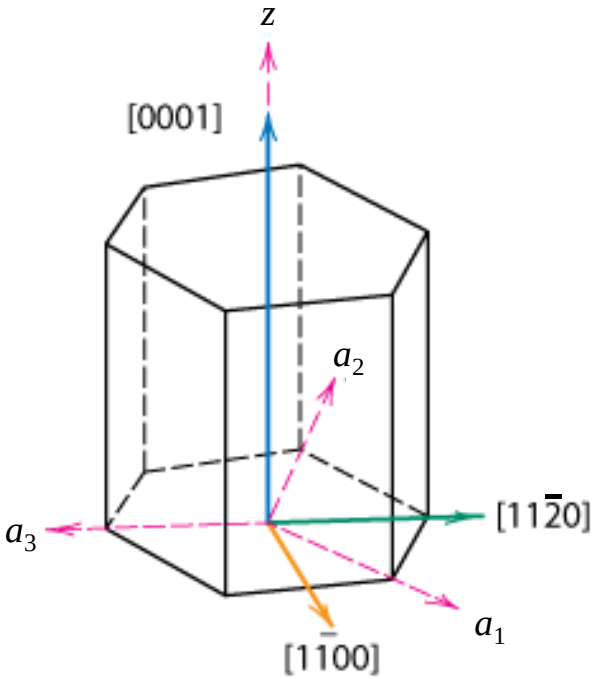


Fig. 3.8(a), *Callister 7e.*

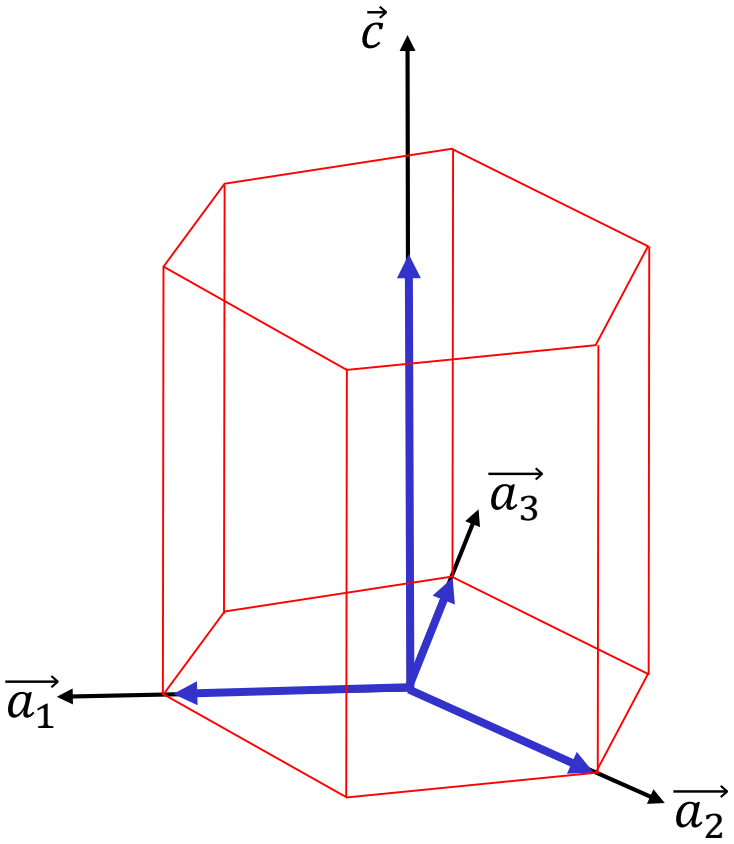
$$[u'v'w'] \rightarrow [uvtw]$$

$$u = \frac{1}{3}(2u' - v')$$

$$v = \frac{1}{3}(2v' - u')$$

$$t = -(u + v)$$

$$w = w'$$


$\vec{c}$
$\overrightarrow{a_3}$
$\overrightarrow{a_1}$
$\overrightarrow{a_2}$

Miller index $[100]$

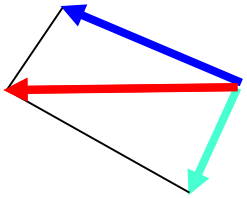
$$u = \frac{1}{3}(2u' - v') \qquad u = \frac{2}{3}$$
$$v = \frac{1}{3}(2v' - u') \qquad v = \frac{-1}{3}$$
$$w = w' \qquad w = 0$$

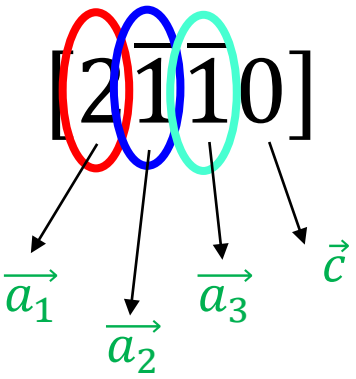
Miller-Bravais index

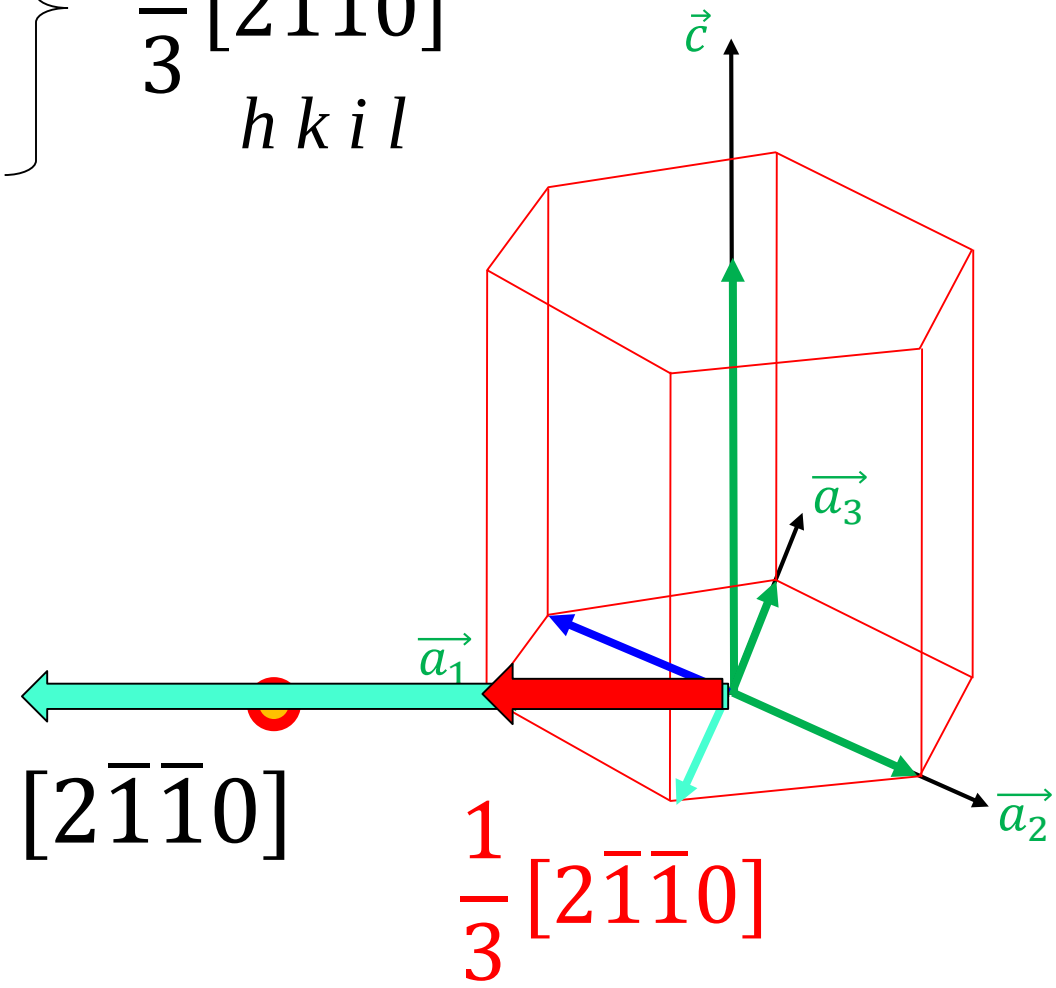
$i=-(h+k)$

$$\frac{1}{3}[2\bar{1}\bar{1}0]$$

$h\ k\ i\ l$





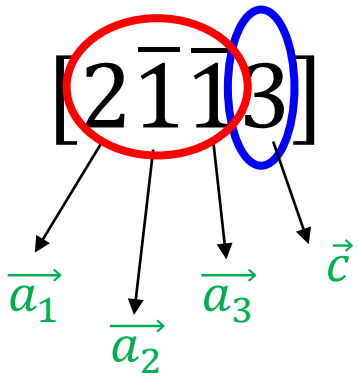


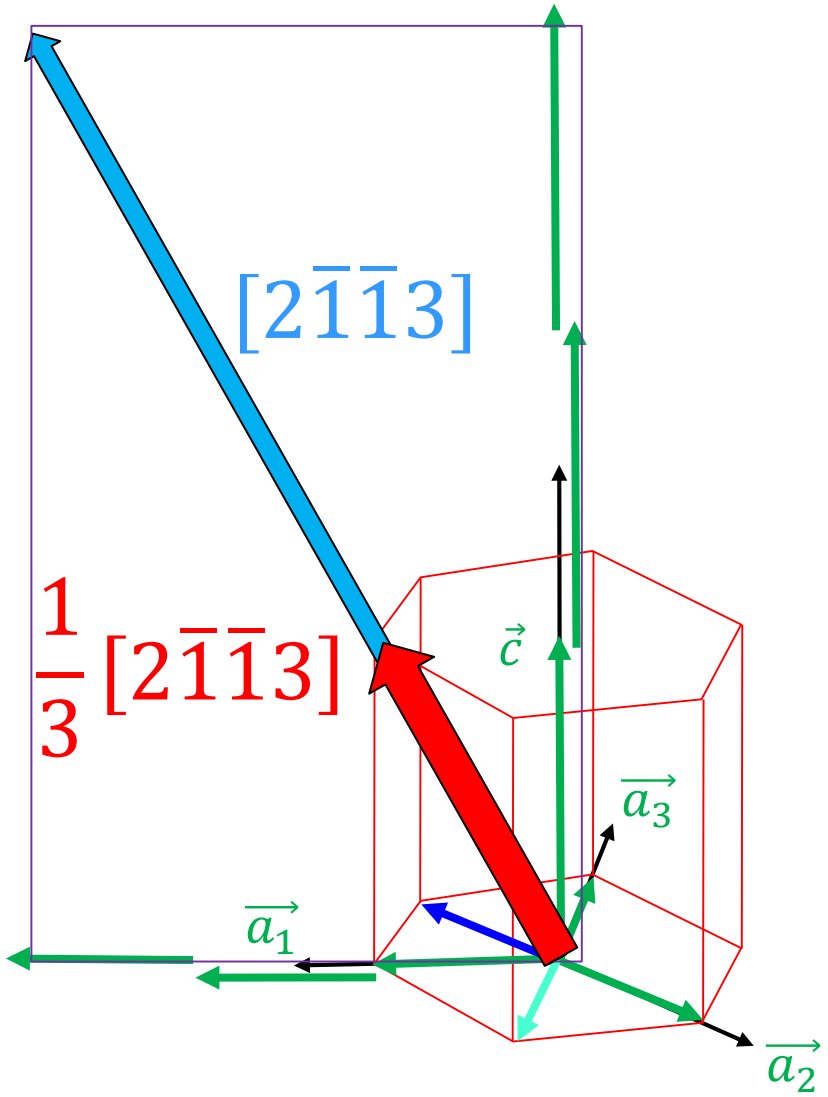
Miller index $[101]$

$$u = \frac{1}{3}(2u' - v') \qquad u = \frac{2}{3}$$
$$v = \frac{1}{3}(2v' - u') \qquad v = \frac{-1}{3}$$
$$w = w' \qquad w = 1$$

Miller-Bravais index

$$\frac{1}{3}[2\bar{1}\bar{1}3]$$





$[2\bar{1}\bar{1}0]$

Miller index

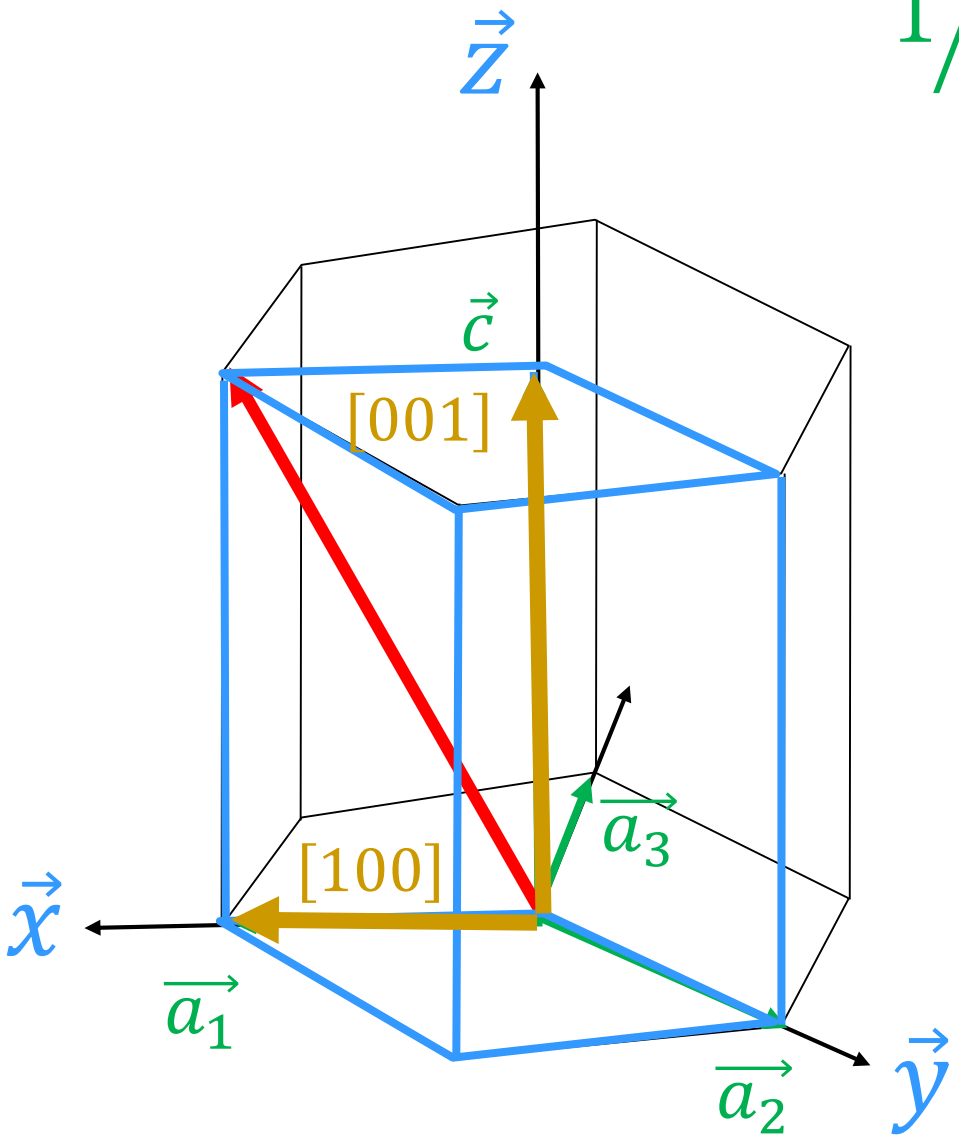
$[101]$

x y z

Miller-Bravais index

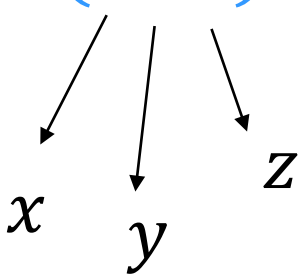
$^1/_3\,[2\bar{1}\bar{1}3]$

$\overrightarrow{a_1}$ $\overrightarrow{a_2}$ $\overrightarrow{a_3}$ $\vec{c}$



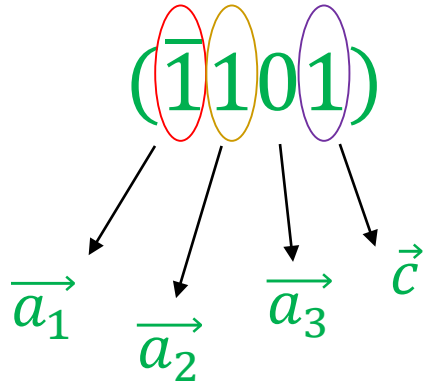
Miller index

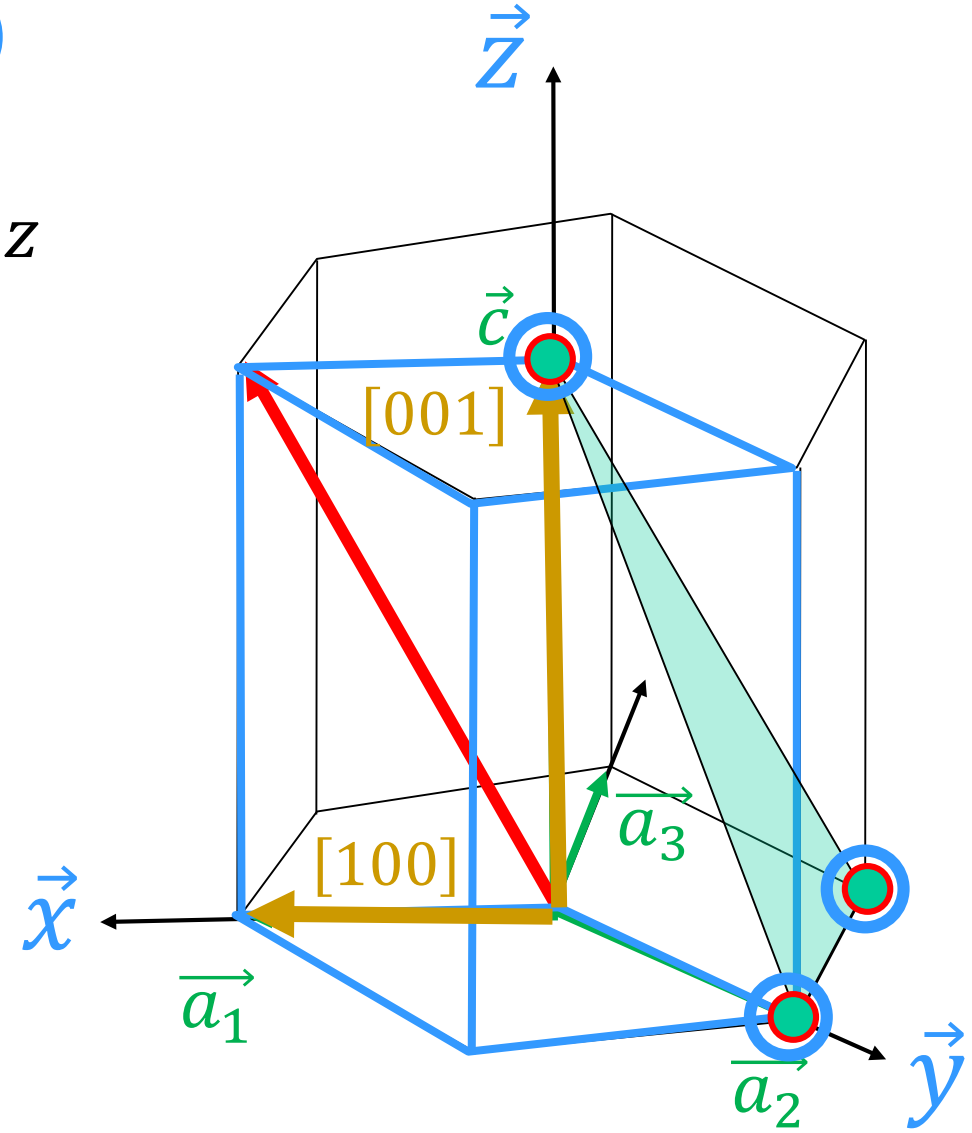
$(\bar{1}11)$



Miller-Bravais index

$(\bar{1}101)$





$$u' = u - t = 2u + v$$

$$v' = v - t = 2v + u$$

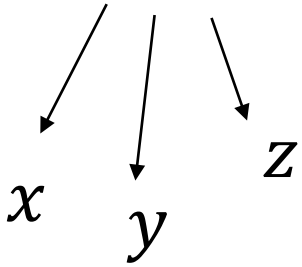
$$w' = w$$

Miller index

$(\bar{1}11)$

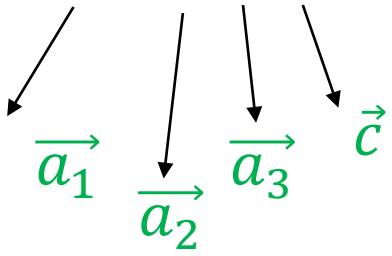
Miller index

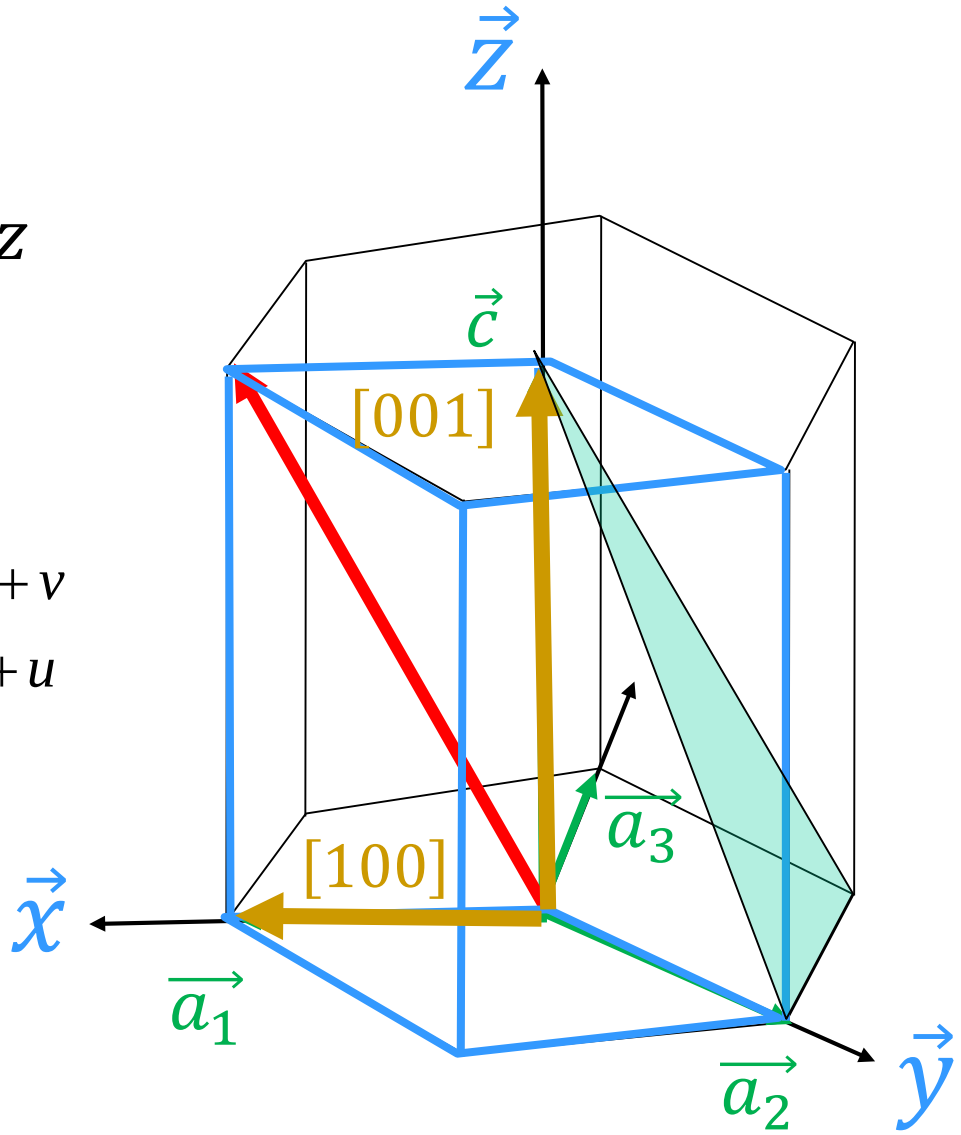
$(\bar{1}11)$



Miller-Bravais index

$(\bar{1}101)$





$$u' = u - t = 2u + v$$

$$v' = v - t = 2v + u$$

$$w' = w$$

$(10\bar{1}0)$

$$u = \frac{1}{3}(2u' - v')$$

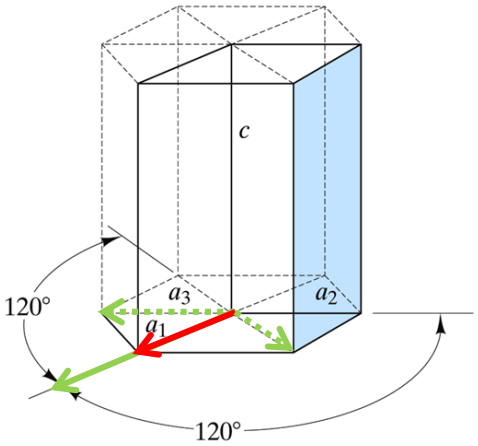
$$v = \frac{1}{3}(2v' - u')$$

$$w = w'$$

Miller-Bravais vs. Miller index system in Hexagonal system

Directions

Miller	Miller–Bravais	Miller	Miller–Bravais
[100]	$[2\bar{1}\bar{1}0]$	[010]	$[\bar{1}2\bar{1}0]$
[110]	[1120]	$[\bar{1}10]$	
[001]	[0001]		
[011]	$[\bar{1}2\bar{1}3]$	[111]	$[11\bar{2}3]$
[210]	$[10\bar{1}0]$	[120]	$[01\bar{1}0]$
[211]	$[10\bar{1}1]$	[112]	$[11\bar{2}6]$



Conversion of 4 index system (Miller-Bravais) to 3 index (Miller)

$$\vec{t} = u'\vec{a}_1 + v'\vec{a}_2 + w'\vec{c} = u\vec{a}_1 + v\vec{a}_2 + t\vec{a}_3 + w\vec{c}$$

Miller-Bravais to Miller
4 to 3 axis

$$u' = u - t = 2u + v$$
$$v' = v - t = 2v + u$$
$$w' = w$$

Miller to Miller-Bravais
3axis to 4 axis system

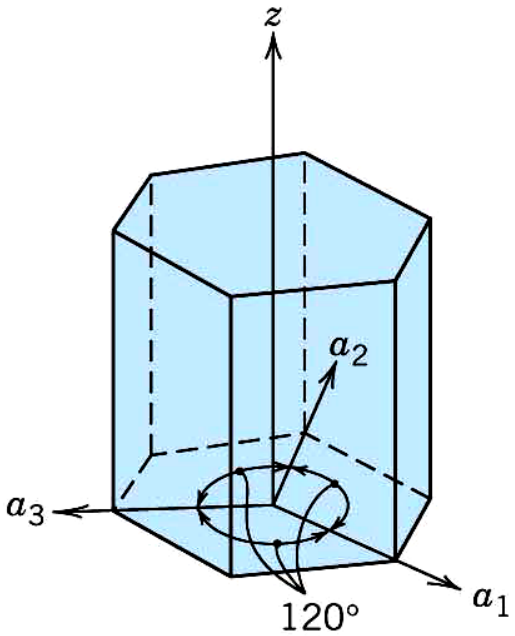
$$u = \frac{1}{3}(2u' - v')$$
$$v = \frac{1}{3}(2v' - u')$$
$$w = w'$$

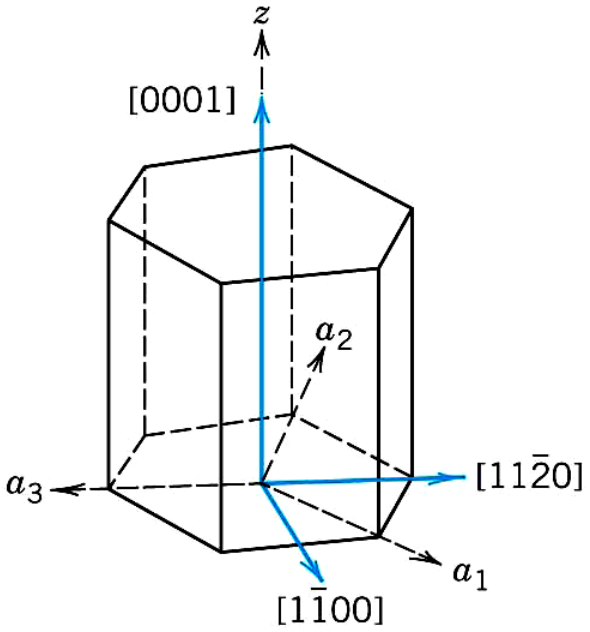
Ex. M [100]
*u=(1/3)(2*1-0)=2/3*
*v=(1/3)(2*0-1)=-1/3*
w=0
=> 1/3[2 -1 -1 0]

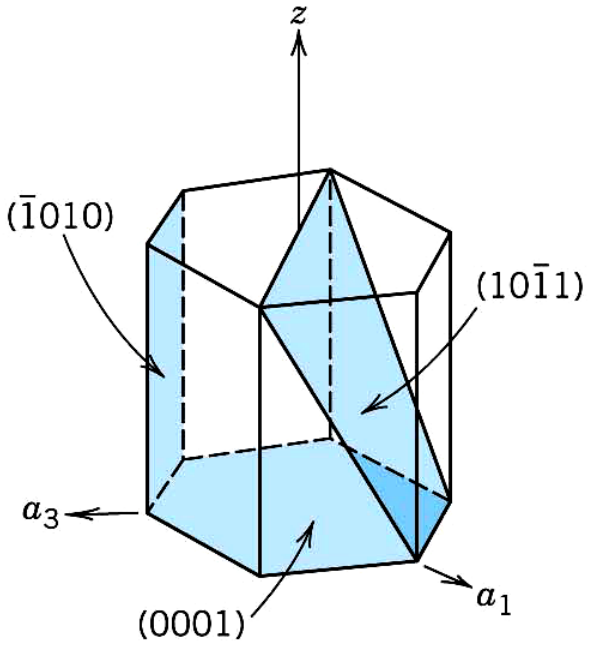
Ex. M-B [1 0 -1 0]
*u'=2*1+0=2*
*v'=2*0+1=1*
w'=0
=> [2 1 0]

Hexagonal Crystal

- **Miller-Bravais scheme**







$$[uvtw] \qquad (hkil)$$

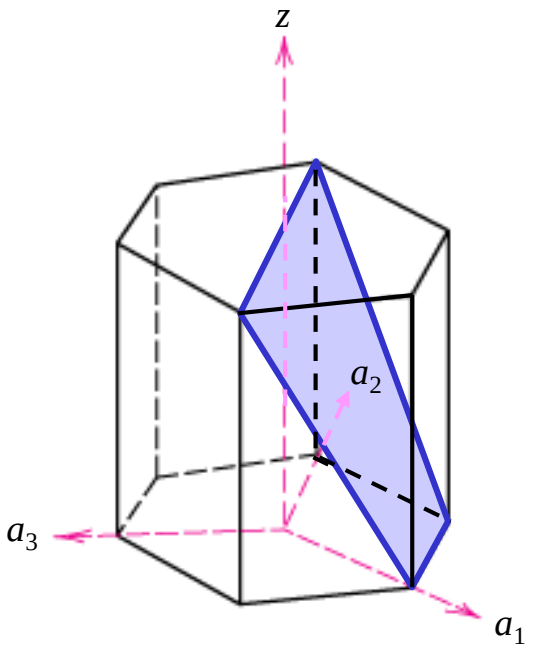
$$t = -(u+v) \qquad i = -(h+k)$$

Crystallographic Planes (HCP)

- **In hexagonal unit cells the same idea is used**

example	a_1	a_2	a_3	c
1. Intercepts	1	∞	-1	1
2. Reciprocals	1	$1/\infty$	-1	1
	1	0	-1	1
3. Reduction	1	0	-1	1

4. Miller-Bravais Indices $(10\bar{1}1)$



Adapted from Fig. 3.8(a), *Callister 7e.*

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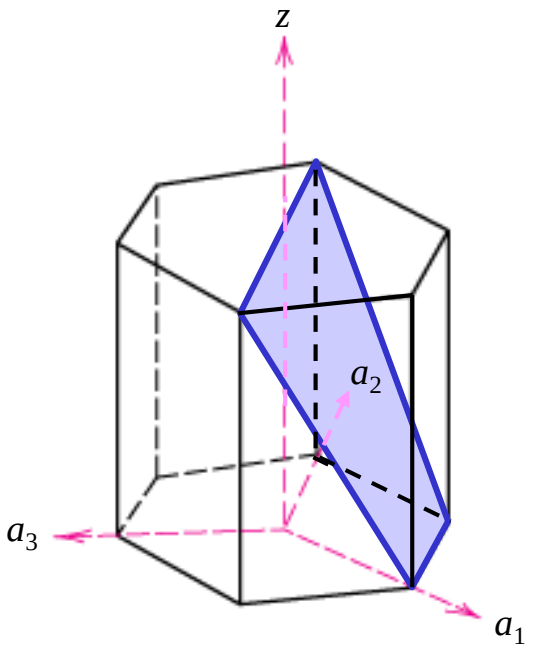
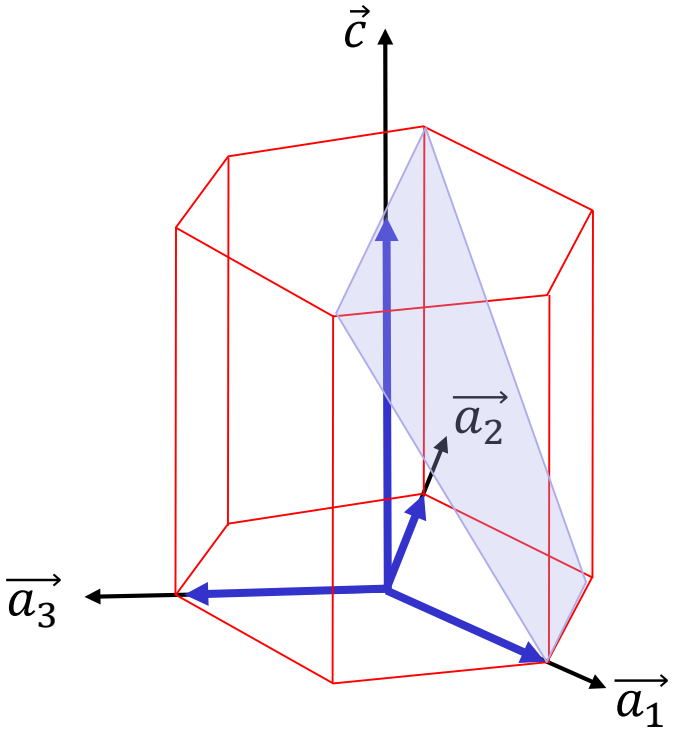


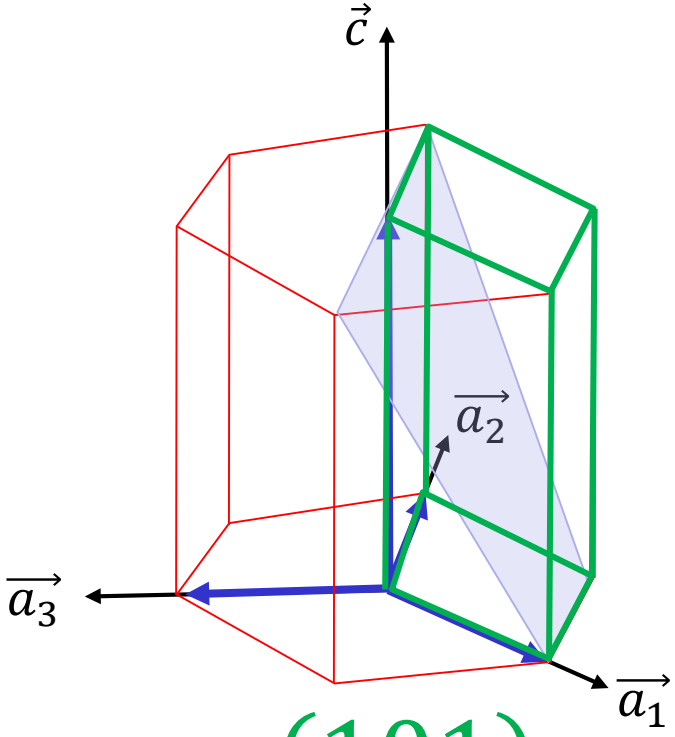
Adapted from Fig. 3.8(a), *Callister 7e.*

Miller-Bravais index



$(10\bar{1}1)$

Miller index



(101)

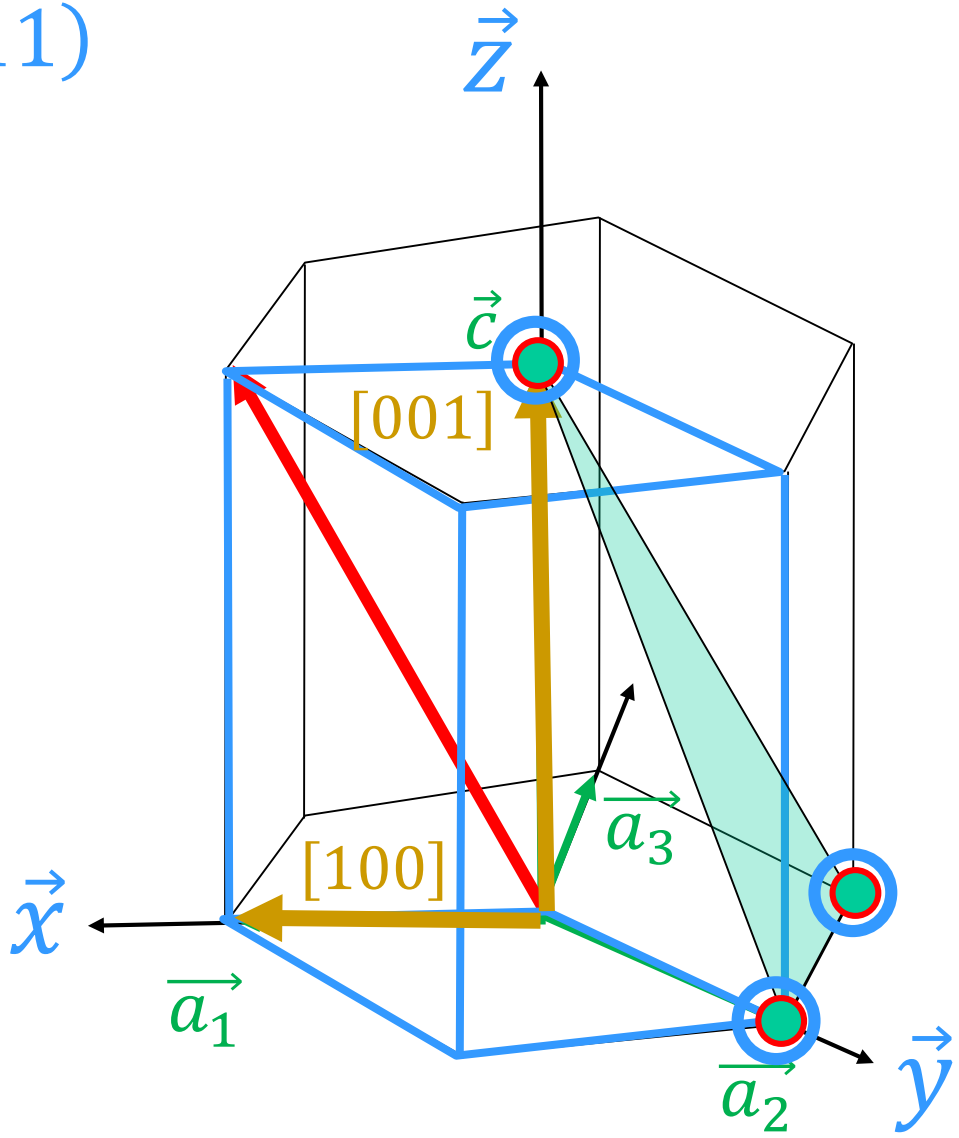
Inverse of 1 =1
Position at $\overrightarrow{a_1}$=1

Inverse of 1 =1
Position at $\vec{c}$ =1

Does not
Meet with $\overrightarrow{a_2}$

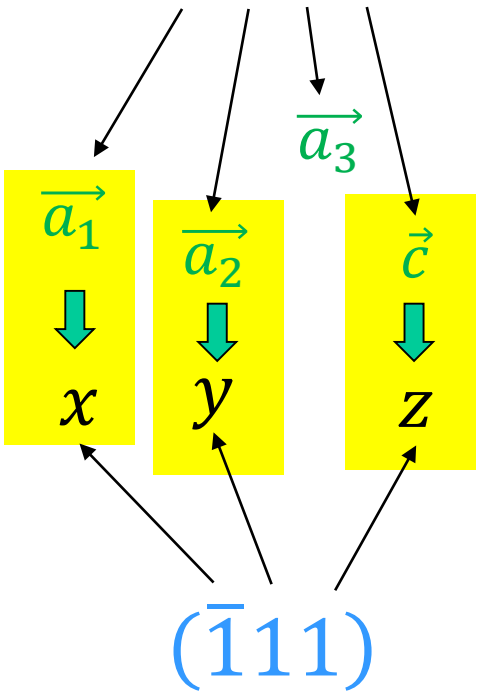
Miller index

$(\bar{1}11)$



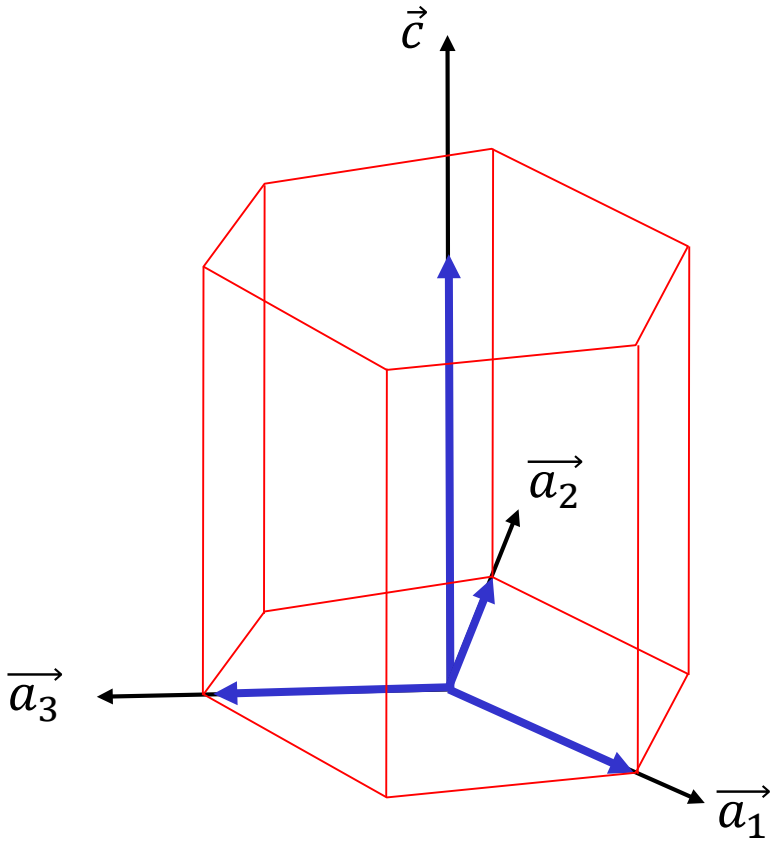
Miller-Bravais index

$(\bar{1}101)$

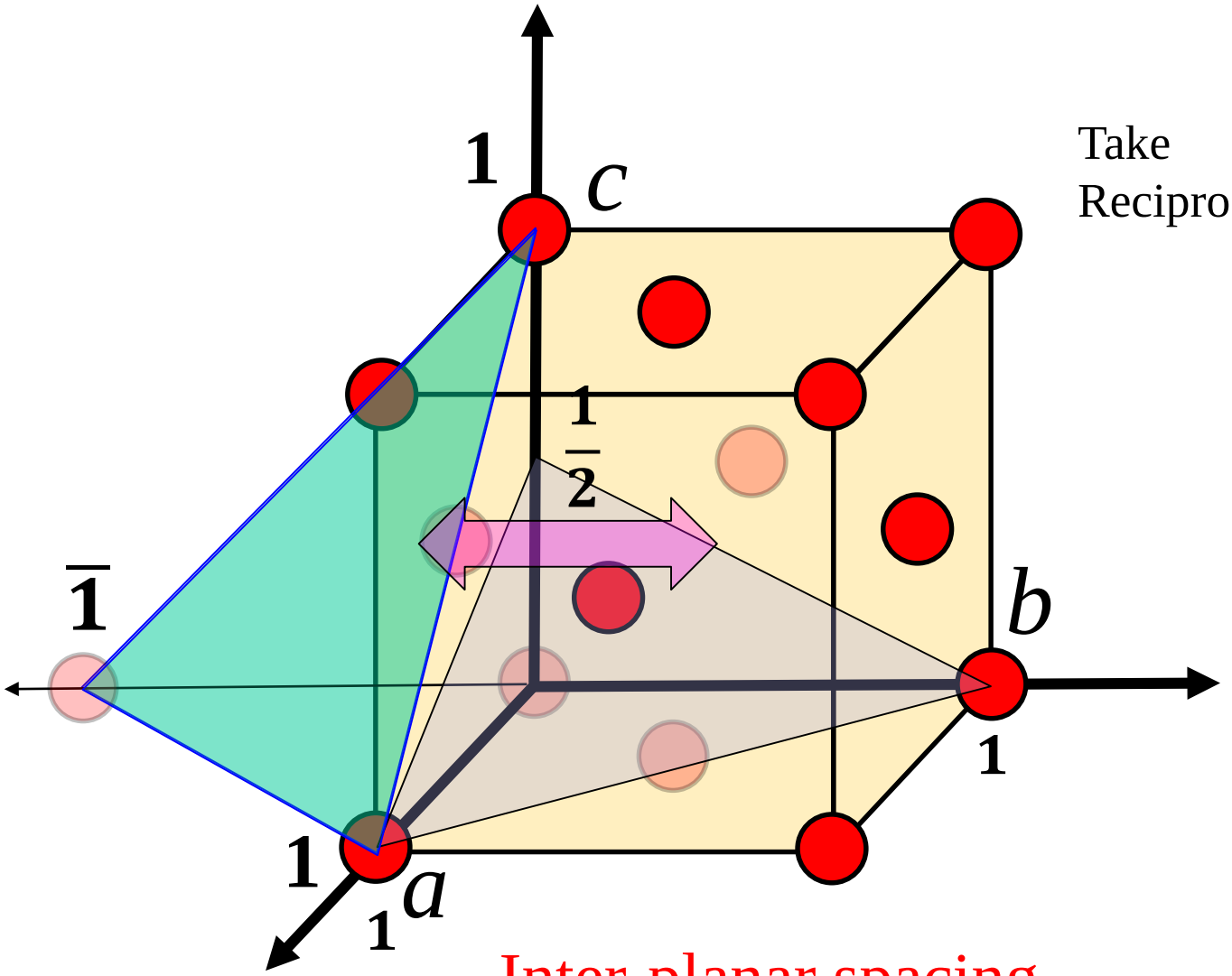


$(\bar{1}11)$

Miller index


$\vec{c}$
$\overrightarrow{a_2}$
$\overrightarrow{a_3}$
$\overrightarrow{a_1}$

Schematic view of planes



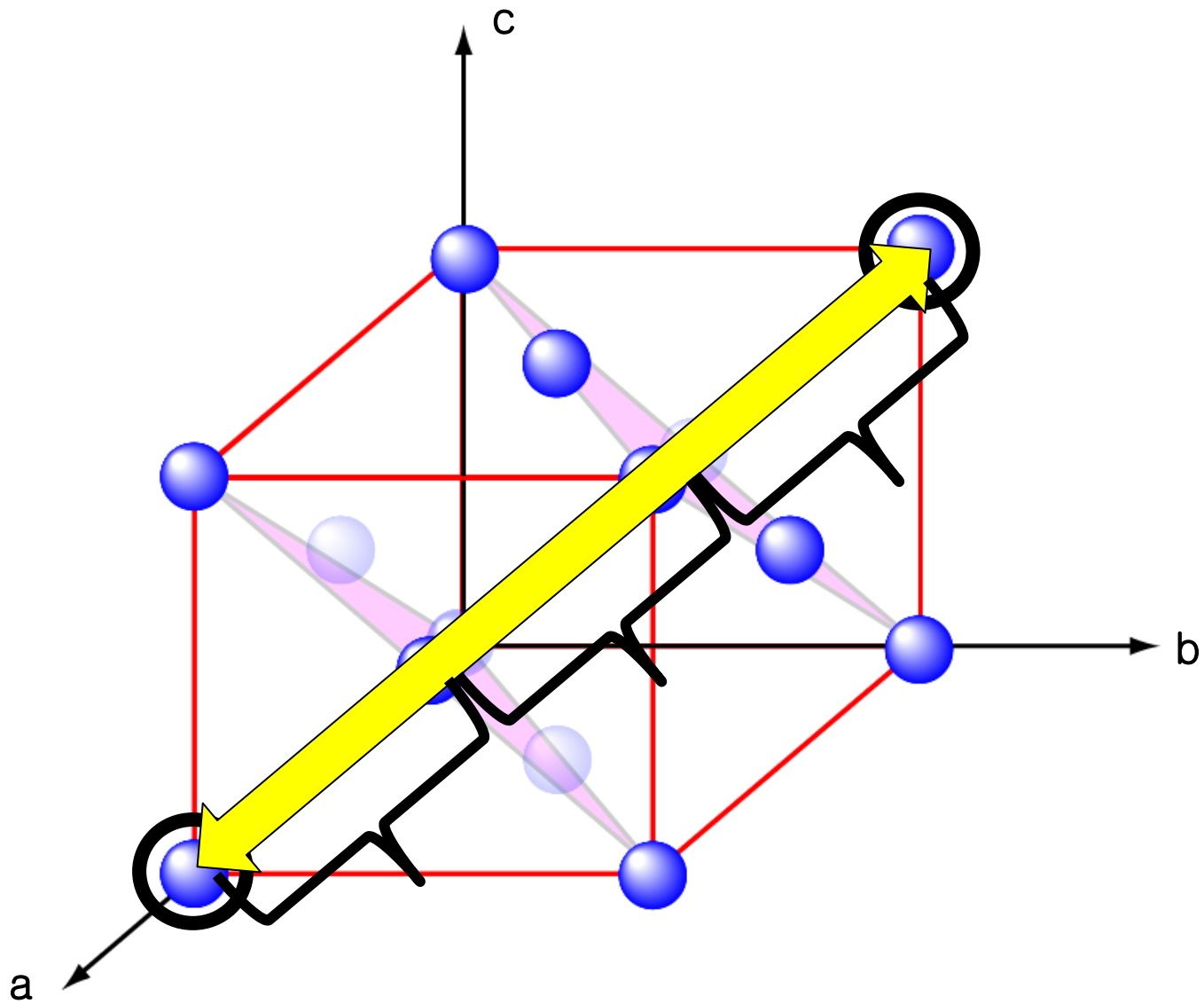
(112)

Take Reciprocal $\Rightarrow 1\ 1\ \frac{1}{2}$

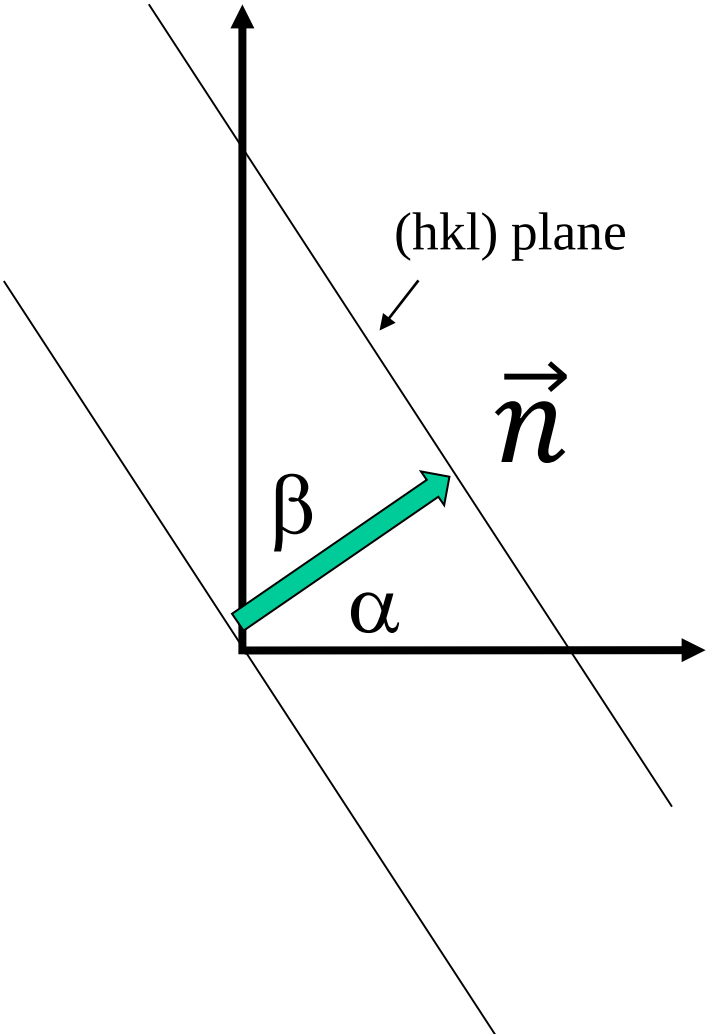
$(1\bar{1}1)$

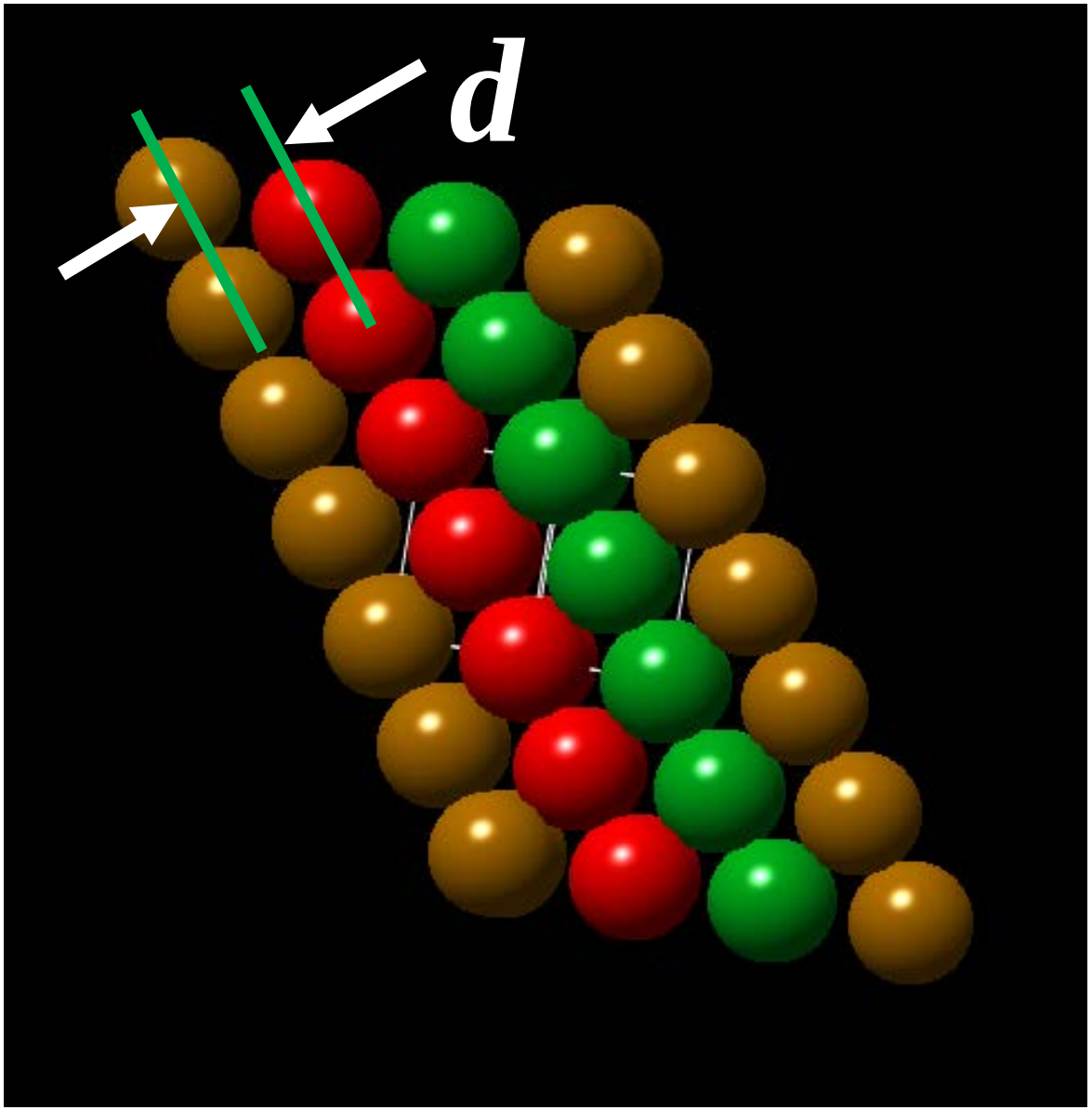
Inter-planar spacing

Schematic view of $(\bar{1}11)$ plane



Inter-planar distance (면간거리)





Interplanar spacing of the (*hkl*) plane

The value of *d* which characterizes the distance between adjacent planes in the set of planes with Miller indices (hkl) is given by the following relations. The cell edges and the angles are *a*, *b*, *c* and α, β ,γ.

Cubic :
$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

Tetragonal :
$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

Orthorhombic :
$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Hexagonal :
$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$$

Rhombohedral :
$$\frac{1}{d^2} = \frac{1}{\sin^2\beta}\left(\frac{h^2}{a^2} + \frac{k^2\sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right)$$

Monoclinic :
$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2)\sin^2\alpha + 2(hk + kl + hl)(\cos^2\alpha - \cos\alpha)}{a^2(1 - 3\cos^2\alpha + 2\cos^3\alpha)}$$

Triclinic :
$$\frac{1}{d^2} = \frac{1}{V^2}(S_{11}h^2 + S_{22}k^2 + S_{33}l^2 + 2S_{12}hk + 2S_{23}kl + 2S_{31}hl)$$

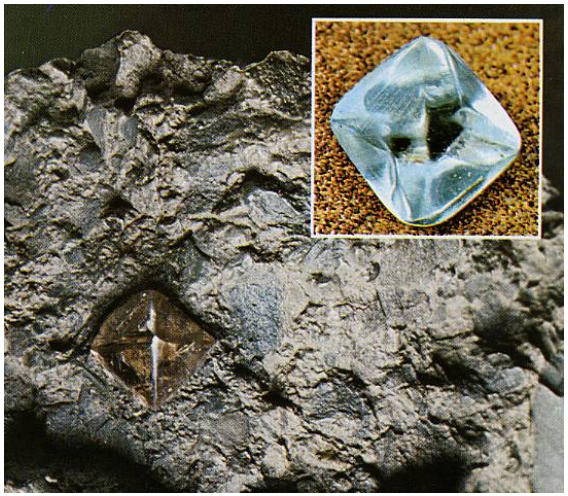
Where :
$$V^2 = a^2b^2c^3(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma)$$

$$S_{11} = b^2c^2\sin^2\alpha$$
$$S_{22} = a^2c^2\sin^2\beta$$
$$S_{33} = a^2b^2\sin^2\gamma$$
$$S_{12} = abc^2(\cos\alpha\cos\beta - \cos\gamma)$$
$$S_{23} = a^2bc(\cos\beta\cos\gamma - \cos\alpha)$$
$$S_{31} = ab^2c(\cos\gamma\cos\alpha - \cos\beta)$$

CRYSTALS AS BUILDING BLOCKS

- ***Some*** **engineering applications require single crystals:**

--diamond single crystals
Natural and artificial



(Courtesy Martin Deakins, GE Superabrasives, Worthington, OH. Used with permission.)

--turbine blades

Fig. 8.30(c), *Callister 6e.* (Fig. 8.30(c) courtesy of Pratt and Whitney).

- **Crystal properties reveal features of atomic structure.**

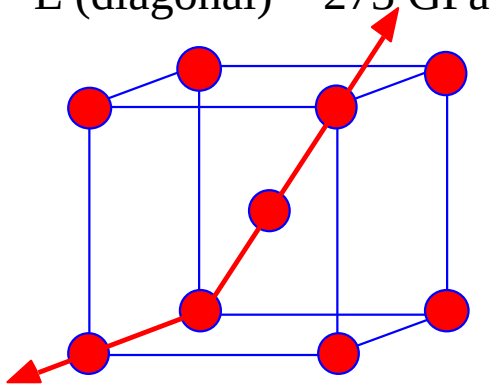
--Ex: Certain crystal planes in quartz fracture more easily than others.

(Courtesy P.M. Anderson)

Single vs Polycrystals

- Single Crystals
  - -Properties vary with direction: anisotropic.
  - -Example: the modulus of elasticity (E) in BCC iron:

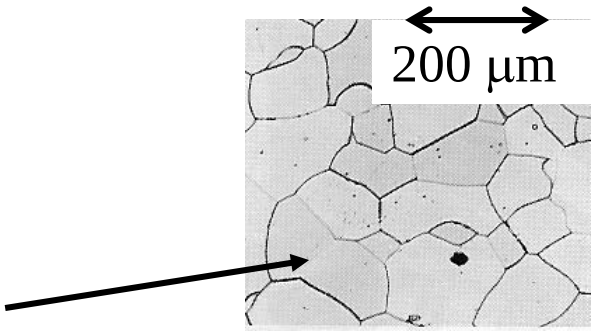
E (diagonal) = 273 GPa

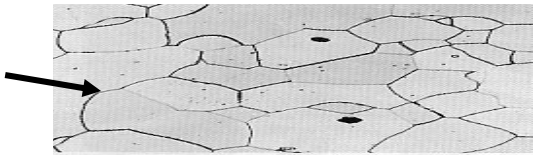


E (edge) = 125 GPa

Data from Table 3.3, *Callister 7e*. (Source of data is R.W. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials*, 3rd ed., John Wiley and Sons, 1989.)

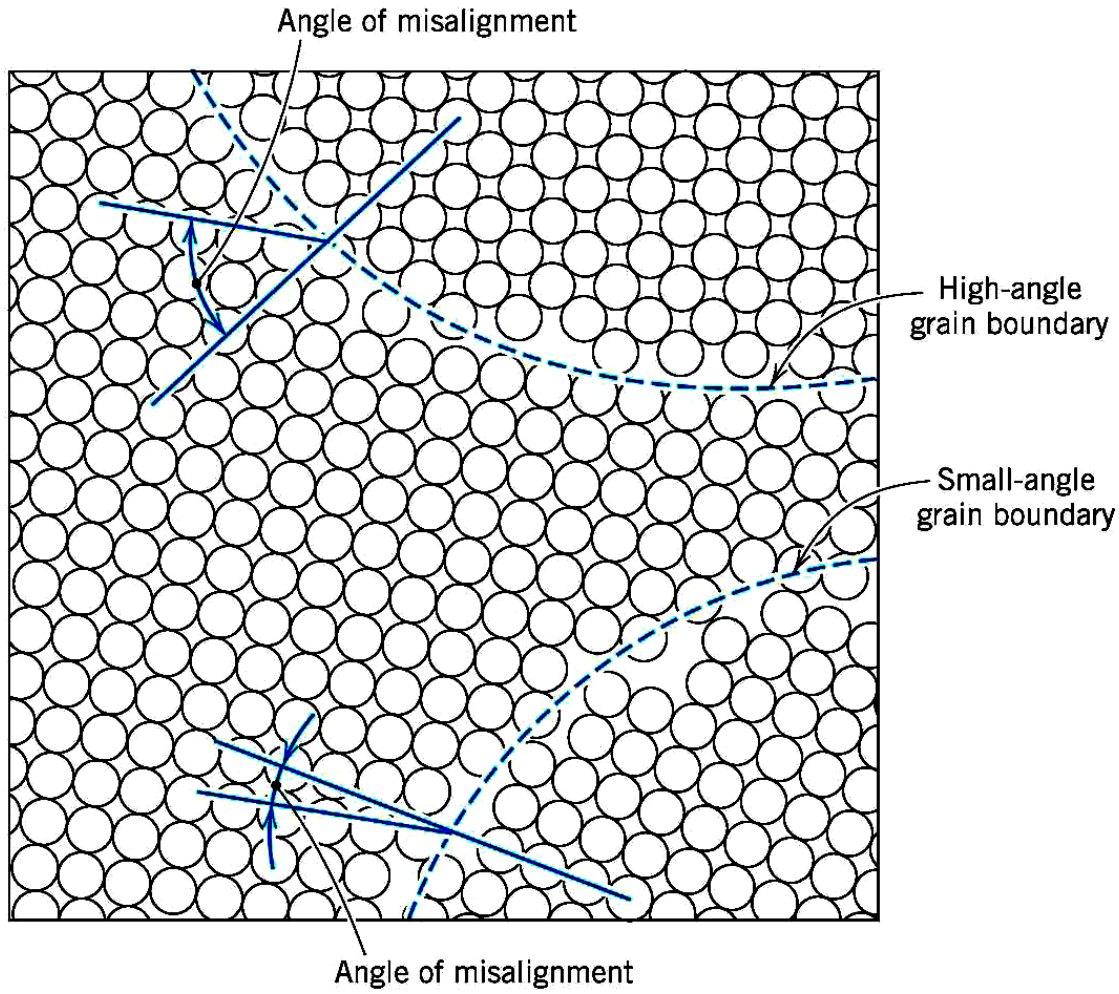
- Polycrystals
  - -Properties may/may not vary with direction.
  - -If grains are randomly oriented: isotropic. ($E_{poly\ iron}$ = 210 GPa)
  - -If grains are textured, anisotropic.

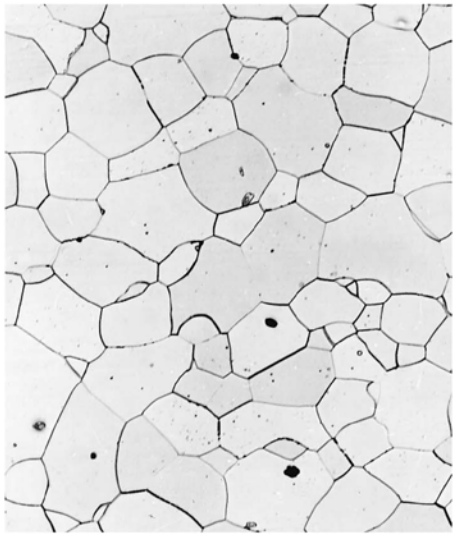


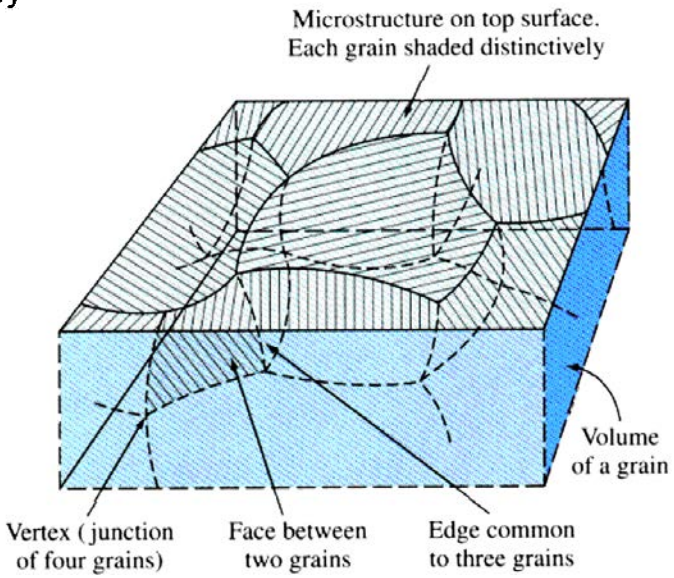


Adapted from Fig. 4.14(b), *Callister 7e*. (Fig. 4.14(b) is courtesy of L.C. Smith and C. Brady, the National Bureau of Standards, Washington, DC [now the National Institute of Standards and Technology, Gaithersburg, MD].)

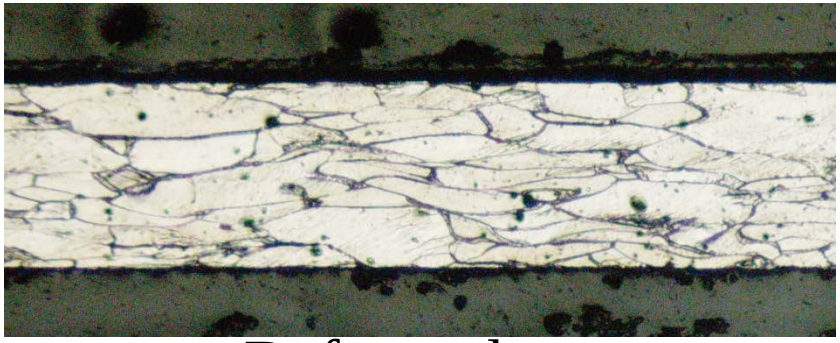
Grain Boundaries



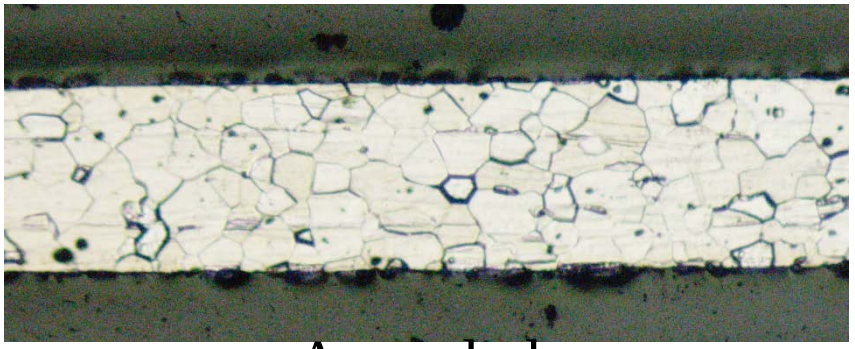




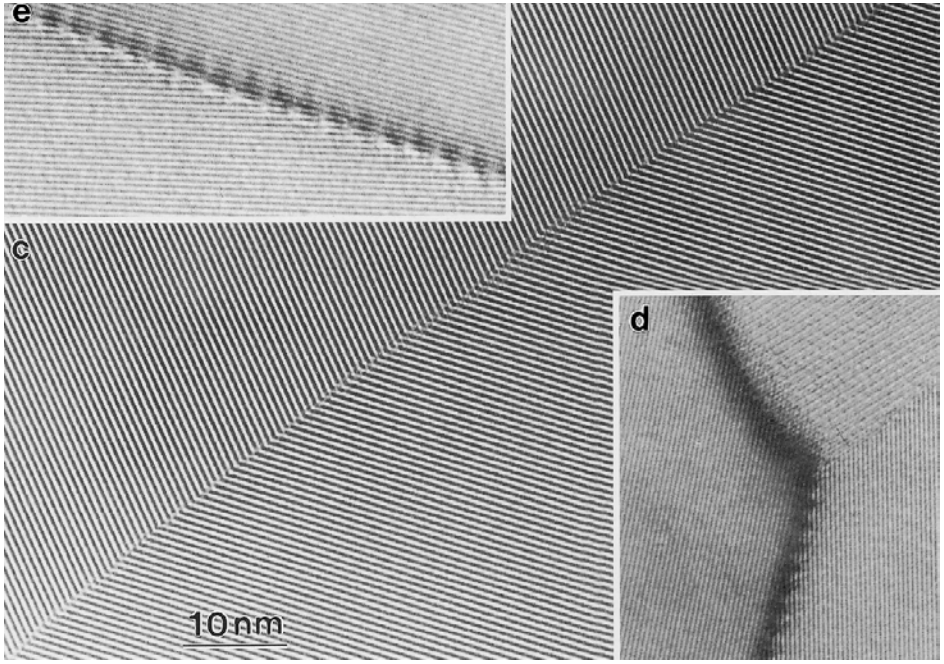
Grains



Deformed



Annealed



Atomic view of grain boundaries

Polycrystals

- *Most* engineering materials are polycrystals.

Anisotropic

Isotropic

Adapted from Fig. K, color inset pages of *Callister 5e*. (Fig. K is courtesy of Paul E. Danielson, Teledyne Wah Chang Albany)

- Nb-Hf-W plate with an electron beam weld.
- Each "grain" is a single crystal.
- If grains are randomly oriented,
  overall component properties are not directional.
- Grain sizes typ. range from 1 nm to 2 cm
  (i.e., from a few to millions of atomic layers).

Polymorphism

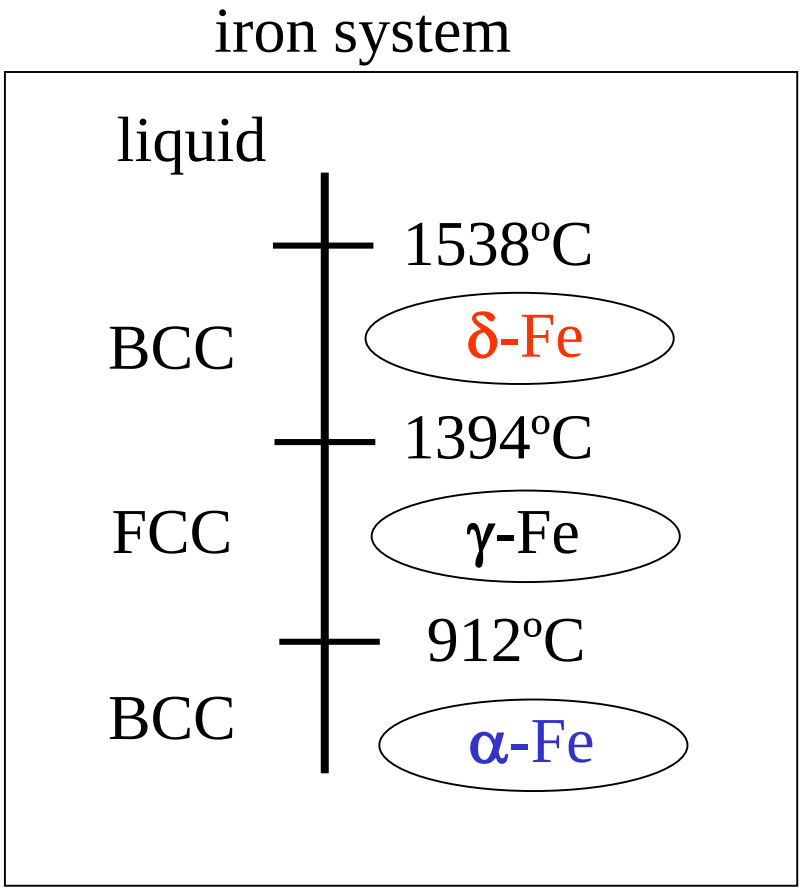
- **Two or more distinct crystal structures for the same material (allotropy/polymorphism)**

titanium

α, β-Ti

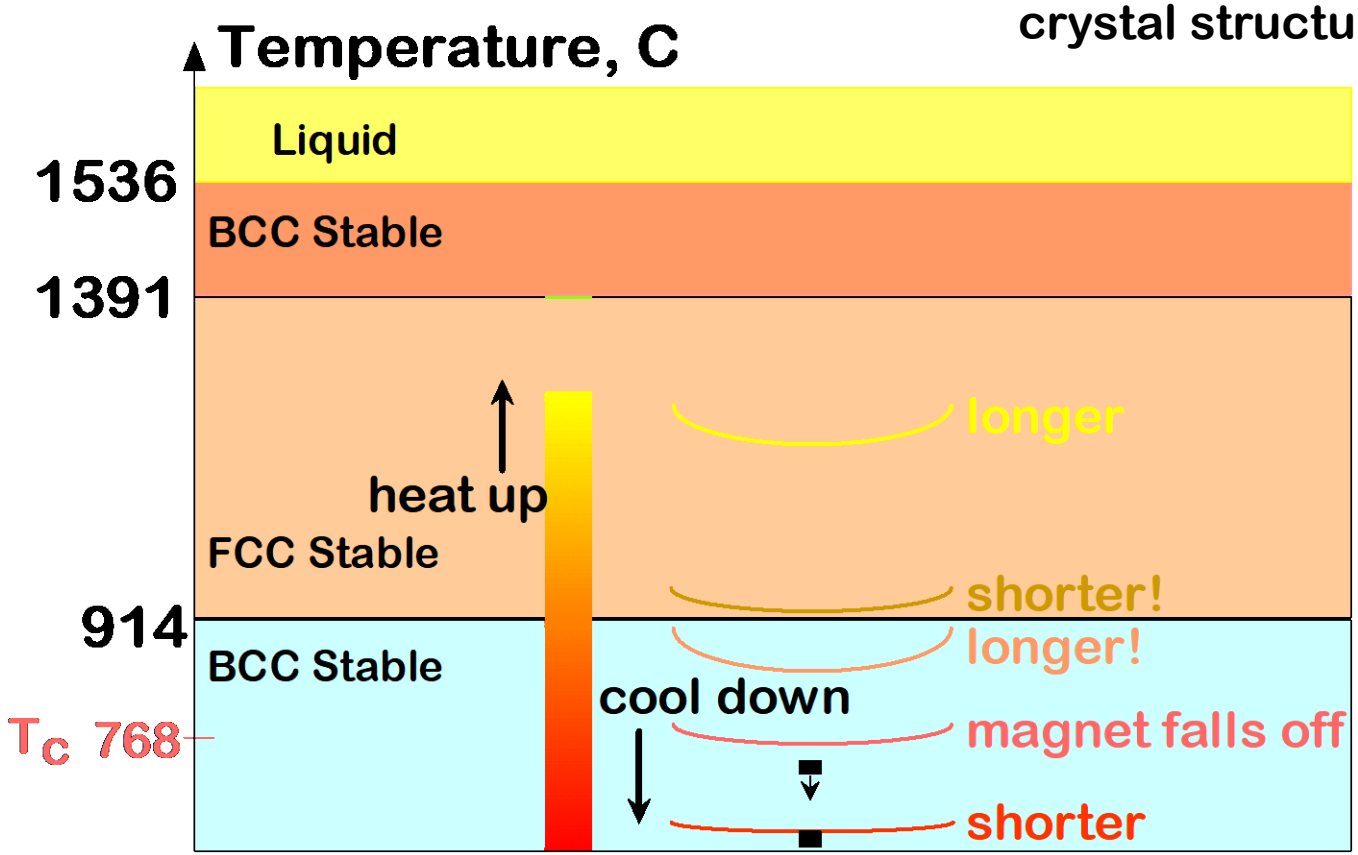
carbon

diamond, graphite



DEMO: HEATING AND COOLING OF AN IRON WIRE

- Demonstrates "polymorphism" ← The same atoms can have more than one crystal structure.



Contents for today's class

CHAPTER 3: Fundamentals of Crystallography

I. Crystal Structures

- Lattice, Unit Cells, Crystal system

II. Crystallographic Points, Directions, and Planes

- Point coordinates, Crystallographic directions, Crystallographic planes

III. Crystalline and Noncrystalline Materials

- Single crystals, Polycrystalline materials, Anisotropy, Noncrystalline solids