MSE 433 and Graduate Class Presentation
Spring Semester
January 24, 2006

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The Figures are mostly from Prof. Kasap’s book but they have been modified and I have added my additional notes as well. I have added my additional notes as well.
Outline - Review of Important Properties Useful In electronic Materials Chapter No. 1

1.1 ATOMIC STRUCTURE
1.2 BONDING AND TYPES OF SOLIDS
1.3 KINETIC MOLECULAR THEORY
1.4 MOLECULAR VELOCITY AND ENERGY DISTRIBUTION
1.5 HEAT, THERMAL FLUCTUATIONS, AND NOISE
1.6 THERMALLY ACTIVATED PROCESSES
1.7 THE CRYSTALLINE STATE
1.8 CRYSTALLINE DEFECTS AND THEIR SIGNIFICANCE
1.9 SINGLE-CRYSTAL CZOCHRAlSKI GROWTH
1.10 GLASSES AND AMORPHOUS SEMICONDUCTORS
1.11 SOLID SOLUTIONS AND TWO-PHASE SOLIDS
**Atomic Orbital and Electron Spin**

**Fig. 1.1:** The shell model of the atom in which the electrons are confined to live within certain shells and in subshells within shells.

1s² 2s² 2p² or [He] 2s² 2p²

**L shell with two subshells**

**Nucleus**

**Fig. 1.2:** The planetary model of the hydrogen atom in which the negatively charged electron orbits the positively charged nucleus.

Stable orbit has radius \( r_o \)


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**Atomic Orbital and Electron Spin**

**VIRIAL THEOREM**
For system that have only Electrostatic Interactions (Attraction and Repulsion)

\[
KE = -\frac{1}{2} PE
\]

**Total Energy of the system** : \( \bar{E} = \bar{KE} + \bar{PE} \)

This Theorem can be applied to Atoms and Molecules

Fig. 1.2: The planetary model of the hydrogen atom in which the negatively charged electron orbits the positively charged nucleus.

Atomic Orbital and Electron Spin (Cont’d)

Ex: Hydrogen Atom

\[
\bar{E} = PE + KE = \frac{1}{2} PE
\]

2. \(\bar{E} = PE \Rightarrow 2 \times (-13.6eV) = 27.2eV\)

Ionization energy for Hydrogen Atom = 13.6 eV

or it takes 13.6 eV to remove electrons to infinity.

\[
KE = \frac{1}{2} PE = 13.6eV
\]

Coulombic Interaction between two charges

\(Q_1 = -e\) and \(Q_2 = +e\) (Charge of nucleus)

separated by a distance \(r_o\): 

\[
PE = \frac{Q_1 \cdot Q_2}{4 \pi \varepsilon_0 \cdot r_o} = -\frac{e + e}{4 \pi \varepsilon_0 \cdot r_o} = -\frac{e^2}{4 \pi \varepsilon_0 \cdot r_o}
\]
**Atomic Orbital and Electron Spin (Cont’d)**

*Ex: Hydrogen Atom:*

\[ r_o = \frac{(1.6 \times 10^{-19} \, C)^2}{4 \pi (8.85 \times 10^{-12} \, F / m)(27.2 \times 1.6 \times 10^{-19} \, J / eV)} \]

\[ r_o = 5.29 \times 10^{-11} \, \text{meters} = 0.0529 \, \text{nm} = 0.00529 \, \text{Angs}. \]

Bohr Radius

\[
\text{KE} = \sqrt{\frac{1}{2} \cdot m_e \cdot \frac{v^2}{}} = \sqrt{\frac{13.6 \times 1.6 \times 10^{-19} \, J / eV}{1/2 \cdot 9.1 \times 10^{-31} \, \text{kg}}} = 2.19 \times 10^{-19} \, \text{m} / \text{s}
\]
Hybridized sp³ Carbon - Diamond 6 electrons

S

Is - 283.9 eV

2sp³ -6.5 eV

Carbon – graphite 6 electrons (non-hybridized)

Is - 283.9 eV

Sodium 11 electrons

Energy (eV)

-283.9

Figure 2.3
Energy-level diagram for the orbital electrons in a C³⁺ ion. Notice the sign convention. An electron's energy is negative. The Is electrons are closer to the nucleus (see Figure 2.1) and more strongly bound (binding energy = -283.9 eV). The outer orbital electrons have a binding energy of only ~6.5 eV. The zero level of binding energy corresponds to an electron completely removed from
the nucleus.

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the nucleus.
Allotropes of Carbon

Diamond Structure

Hybridized sp³ Carbon - Diamond 6 electrons

Graphite Structure

Carbon – graphite 6 electrons (non-hybridized)

K Shell

L Shell

M Shell

All are Carbon atoms
One More Allotrope of Carbon

(a) Diamond unit cell

Covalently bonded network of atoms
Cubic crystal

(b) Graphite

Layers bonded by van der Waal bonding
Covalently bonded layer
Hexagonal unit cell

(c) Buckminsterfullerene

The FCC unit cell of the Buckminsterfullerene crystal. Each lattice point has a $\text{C}_{60}$ molecule

Buckminsterfullerene ($\text{C}_{60}$) molecule (the "buckyball" molecule)

Fig. 1.42: The three allotropes of carbon.

Types of Bonds

• PRIMARY BONDS - 3
  Ionic Bond ..... Ex: NaCl
  Covalent Bond .... Ex: Diamond, Si, Ge,
  Metallic Bond ..... Ex: Al, Ni, Au
  Mixed Ionic and Covalent

• SECONDARY BONDS
  Fluctuating Dipole Bond — Observed in Noble gases He
  Permanent Dipole Bond – Observed in Ice (O-H…O Bond)
IONIC BONDING

Ionic Bonding In NaCl

Fig. 1.8: The formation of an ionic bond between Na and Cl atoms in NaCl. The attraction is due to coulombic forces.


Ionic Bonding of Mg and Cl₂ results in formation of MgCl₂. The Mg atom gives up two electrons from it's valence shell to completely fill completely the Cl shell (that lacks one electron) to make MgCl₂, compound

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<th></th>
<th>CI</th>
<th>Mg⁺⁺⁺</th>
<th>CI⁻</th>
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<td>12</td>
<td>17</td>
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<tr>
<td>Electrons</td>
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<td>10</td>
<td>18</td>
</tr>
<tr>
<td>Neutrons</td>
<td>17</td>
<td>12</td>
<td>17</td>
</tr>
<tr>
<td>Size of Neutral Atoms</td>
<td>~3.6 A</td>
<td>~1.6 A</td>
<td>~3.6 A</td>
</tr>
<tr>
<td>Net Charge on Atom</td>
<td>-1</td>
<td>+2</td>
<td>-1</td>
</tr>
</tbody>
</table>
Fig. 1.9: (a) A schematic illustration of a cross section from solid NaCl. NaCl solid is made of Cl\(^{-}\) and Na\(^{+}\) ions arranged alternatingly so that the oppositely charged ions are closest to each other and attract each other. There are also repulsive forces between the like-ions. In equilibrium the net force acting on any ion is zero. (b) Solid NaCl.
**ATTRACTIVE and REPULSIVE FORCES IN BONDING**

\[
F_c \text{ attr.} = \frac{K}{a^2} = 2.98 \times 10^{-9} \text{ N}
\]

**Figure 2.6**

*Plot of the coulombic force (Equation 2.1) for a Na⁺–Cl⁻ pair.*

**Figure 2.7**

*Force curve for a Na⁺–Cl⁻ pair with equilibrium bond length of \(a_0 = 0.28 \text{ nm}.*

\[
k_0 = 9 \times 10^9 (V.m/C)
\]

\(z_1 = \text{Charge of Na}^+ = +1\)

\(z_2 = \text{Charge of Cl}^- = -1\)

\(q_1 = q_2 = 0.16 \times 10^{-18} \text{ C}\)

\(\text{r}_1 = \text{Na Radius} = 0.098 \text{ nm}\)

\(\text{r}_2 = \text{Cl Radius} = 0.181 \text{ nm}\)

\(a = 0.278 \text{ nm}\)

\[
K = [-k_0 (z_1z_2)^2Q_1Q_2] = -k_0 (z_1z_2)^2(Q)^2
\]

\[
\begin{align*}
(V.m/C)(+1)^2.C(-1)^2.C &= \frac{VC}{m} = N.m = N.m^2 \\
1 \text{ Pascal} &= 1 \text{ N/m}^2 = 1 \text{ J} = N.m \\
1 \text{ V.C} &= 1 \text{ J} = N.m
\end{align*}
\]
Inter-atomic Force and Energy in a Crystal

(a) Force vs $r$

- $F_A$ = Attractive force
- $F_R$ = Repulsive force
- $F_N$ = Net force
- $r_o$ = Interatomic separation
- $r$ = Separated atoms

(b) Potential energy vs $r$

- $E_A$ = Attractive $PE$
- $E_R$ = Repulsive $PE$
- $E$ = Net $PE$
- $r_o$ = Interatomic separation
- $E_o$ = Potential energy

Fig. 1.3: (a) Force vs interatomic separation and (b) Potential energy vs interatomic separation.

Fig. 1.4: Formation of a covalent bond between two H atoms leads to the H₂ molecule. Electrons spend majority of their time between the two nuclei which results in a net attraction between the electrons and the two nuclei which is the origin of the covalent bond.


Fig. 1.5: (a) Covalent bonding in methane, CH₄, involves four hydrogen atoms sharing electrons with one carbon atom. Each covalent bond has two shared electrons. The four bonds are identical and repel each other. (b) Schematic sketch of CH₄ on paper. (c) In three dimensions, due to symmetry, the bonds are directed towards the corners of a tetrahedron.

Covalent Bonds - Crystal Structure of Diamond

Fig. 1.6: The diamond crystal is a covalently bonded network of carbon atoms. Each carbon atom is bonded covalently to four neighbors forming a regular three dimensional pattern of atoms which constitutes the diamond crystal.

Metallic Bonds

Electrons are delocalized and form electron cloud
Can bond the atoms
These electron can carry current or heat

Free valence electrons forming an electron gas
Positive metal ion cores

Metallic bond consisting of an electron cloud, or gas.
An imaginary slice is shown through the front face of the crystal structure of copper, revealing Cu\(^{2+}\) ion cores bonded by the delocalized valence electrons.

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<th>Heat of sublimation</th>
<th>Metal oxide</th>
<th>Heat of sublimation</th>
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<tr>
<td></td>
<td>kcal/mol</td>
<td>kJ/mol</td>
<td>kcal/mol</td>
</tr>
<tr>
<td>Al</td>
<td>78</td>
<td>326</td>
<td>FeO</td>
</tr>
<tr>
<td>Cu</td>
<td>81</td>
<td>338</td>
<td>MgO</td>
</tr>
<tr>
<td>Fe</td>
<td>100</td>
<td>416</td>
<td>α-TiO</td>
</tr>
<tr>
<td>Mg</td>
<td>35</td>
<td>148</td>
<td>TiO(_2) (rutile)</td>
</tr>
</tbody>
</table>

Fig. 1.7: In metallic bonding the valence electrons from the metal atoms form a "cloud of electrons" which fills the space between the metal ions and "glues" the ions together through the coulombic attraction between the electron gas and positive metal ions.

Bond Energies for NaCl

Fig. 1.10: Sketch of the potential energy per ion-pair in solid NaCl. Zero energy corresponds to neutral Na and Cl atoms infinitely separated.

Energy/ion $\text{Na}^+\text{Cl}^- = 6.3/2 = 3.15$ eV
Energy Req'd. To Solid Atoms apart = Cohesive Energy = 3.15 eV per atom

Fig. 1.11: (a) A permanently polarized molecule is called a an electric dipole moment. (b) Dipoles can attract or repel each other depending on their relative orientations. (c) Suitably oriented dipoles attract each other to form van der Waals bonds.
**O-H…O Secondary Van der Waal Bonds In Ice and Water**

![Diagram](image)

**Fig. 1.12:** The origin of van der Waals bonding between water molecules. (a) The H₂O molecule is polar and has a net permanent dipole moment. (b) Attractions between the various dipole moments in water gives rise to van der Waals bonding.

**Fluctuating Van der Waal Bonds In Gas Cooled to Very Low Temperatures**

Time averaged electron (negative charge) distribution

Closed $L$ Shell

Ionic core (Nucleus + $K$-shell)

Ne

Instantaneous electron (negative charge) distribution fluctuates about the nucleus.

Synchronized fluctuations of the electrons

Fig. 1.13: Induced dipole-induced dipole interaction and the resulting van der Waals force.

Calculations of Bond Energy and Equilibrium distance between atoms for Secondary Bonds

*Lennard – Jones 6–12 Potential*

\[ E(r) = -Ar^{-6} + Br^{-12} \]

\[ A = 8 \times 10^{-27} \text{ J.m}^6 \]

\[ B = 1.12 \times 10^{-13} \text{ J.m}^{12} \]

\[ \frac{dE}{dr} = 6Ar^{-7} + 12Br^{-13} = 0 \quad @ r = r_o \]

\[ r_o = \left[ \frac{2B}{A} \right]^{1/6} \]

Substituting A and B, solve for \( r_o \)

\[ r_o = 3.75 \times 10^{-10} \text{ m} = 0.375 \text{ nm} \]

Thus \( @r_o = 3.75 \times 10^{-10} \text{ m} \ldots \text{The Potential Energy PE is minimum} \)

and is \( E_{\text{bond}} = \left| -Ar_o^{-6} + Br_o^{-12} \right| = 1.43 \times 10^{-20} \text{ Joules} \)

*Also* \( E_{\text{bond}} = 0.089 \text{ eV} \ldots \text{Small when Compared to the Primary Energies.} \)
Elastic Forces and Young’s Modulus

Elastic Modulus $Y = \frac{\sigma}{\epsilon} = \frac{1}{r_o} \left( \frac{dF_n}{dr} \right)_{r=r_o} = \frac{1}{r_o} \left( \frac{d^2 E}{dr^2} \right)_{r=r_o}$

$Y = f \cdot \frac{E_{Bond}}{(r_o^3)}$ ........ $f \sim 1$ ............ Numerical Constant

Fig. 1.14: (a) Applied forces $F$ stretch the solid elastically from $L_o$ to $\delta L$. The force is divided amongst chains of atoms that make the solid. Each chain carries a force $\delta F_N$. (b) In equilibrium, the applied force is balanced by the net force $\delta F_N$ between the atoms as a result of their increased separation.

**Kinetic Theory**

Fig. 1.15: The gas molecules in the container are in random motion.


\[ P = \frac{m \cdot N \cdot \overline{v_x}^2}{V} \]

\[ \overline{v_x}^2 = \text{Mean Square Velocity} \]

\[ V = \text{Volume} = a^3 \]

\[ m = \text{Mass of Atom or molecule} \]

\[ v = \text{Velocity} \]

Total Pressure Exerted by \( n \) Molecules to the walls of the Cube = \( P \)

Gas Pressure = \[ \frac{m \cdot N \cdot \overline{v^2}}{3 \cdot V} = \frac{1}{3} \rho \cdot \overline{v^2} \]

\[ \ldots \ldots \ldots \rho = \text{Density of Gas} \]
Kinetic Theory

Mean Kinetic Energy / Atom = $\overline{KE} = \frac{1}{2} \cdot m \cdot v^2 = \frac{3}{2} \cdot k \cdot T$

$k = $ Boltzmann Constant

Internal … Energy of monotonic Gas = $\frac{3}{2} \cdot N_A \cdot kT = N_A \cdot \frac{1}{2} \cdot m \cdot v^2$

Molar … Heat Capacity (Constant Volume) = $\frac{dU}{dT} = \frac{3}{2} \cdot N_A \cdot k = \frac{3}{2} \cdot R$
Fig. 1.16: Possible translational and rotational motions of a diatomic molecule. Vibrational motions are neglected.

MSE 433 and Graduate Class Presentation
Spring Semester

2nd. Lecture

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Atomic Vibrations – Spring Model – 3D Motion as Proposed by Debye

Fig. 1.17 (a) The ball-and-spring model of solids in which the springs represent the interatomic bonds. Each ball (atom) is linked to its neighbors by springs. Atomic vibrations in a solid involve 3 dimensions. (b) An atom vibrating about its equilibrium position stretches and compresses its springs to the neighbors and has both kinetic and potential energy.

Internal Energy, \( U = N_A \cdot 6 \cdot \left( \frac{1}{2} \cdot kT \right) = 3R \)

Dulong and Petit Rule:

\[ C_m = \frac{dU}{dT} = 3R = 25 \text{ J/mol.K} \]

**Thermal Expansion in Solids**

**Fig. 1.18:** The potential energy $PE$ curve has a minimum when the atoms in the solid attain the interatomic separation at $r = r_o$. Due to thermal energy, the atoms will be vibrating and will have vibrational kinetic energy. At $T = T_1$, the atoms will be vibrating in such a way that the bond will be stretched and compressed by an amount corresponding to the $KE$ of the atoms. A pair of atoms will be vibrating between $B$ and $C$. Their average separation will be at $A$ and greater than $r_o$.

**Fig. 1.19:** Vibrations of atoms in the solid. We consider, for simplicity a pair of atoms. Total energy is $E = PE + KE$ and this is constant for a pair of vibrating atoms executing simple harmonic motion. At $B$ and $C$, $KE$ is zero (atoms are stationary and about to reverse direction of oscillation) and $PE$ is maximum.
Thermal Expansion Coefficient vs Temperature Plot

Compare W, Mo (Refractory Metals) with Si (Semiconductor)

Figure 1.20 Dependence of the linear thermal expansion coefficient $\alpha$ (K$^{-1}$) on temperature $T$ (K) on a log-log plot.

HDPE, high-density polyethylene; PMMA, polymethylmethacrylate (acrylic); PC, polycarbonate; PET, polyethylene terephthalate (polyester); fused silica, SiO$_2$; alumina, Al$_2$O$_3$.

Determination of Molecular Speed Distribution

Stern Type Experiment

Fig. 1.21 Schematic diagram of a Stern type experiment for determining the distribution of molecular speeds.

Fig. 1.21: Maxwell-Boltzmann distribution of molecular speeds in nitrogen gas at two temperatures. The ordinate is $dN/(Ndv)$, the fractional number of molecules per unit speed interval in (km/s)$^{-1}$

Energy, $E$

Average KE at $T_1$.

Average KE at $T_2$

$T_2 > T_1$

$E_A$

Energy, $E$

$\exp(-E_A/kT)$

**Fig. 1.23** Energy distribution of gas molecules at two different temperatures. The number of molecules that have energies greater than $E_A$ is the shaded area. This area depends strongly on the temperature as $\exp(-E_A/kT)$.

During collisions between the gas and solid atoms, kinetic energy is exchanged.

Fig. 1.25: Fluctuations of a mass attached to a spring due to random bombardment by air molecules

http://MaterialsUsask.Ca
Fermi Gas or Electron Random Motion in a Conductor

Random motion of conduction electrons in a conductor results in electrical noise.

Charge Discharge of Capacitor

**Fig. 1.26** Charging and discharging of a capacitor by a conductor due to the random thermal motions of the conduction electrons.


http://MaterialsUsaskCa
Comparison of Stable and Meta-stable States in a Solid

\[ U(X) = PE = mgh \]

System Coordinate, \( X = \) Position of Center of Mass

**Fig. 1.27**: Tilting a filing cabinet from state A to its edge in state A* requires an energy \( E_A \). After reaching A*, the cabinet spontaneously drops to the stable position B. PE of state B is lower than A and therefore state B is more stable than A.

**Activation Barrier in Diffusion**

**Fig. 1.28** Diffusion of an interstitial impurity atom in a crystal from one void to a neighboring void. The impurity atom at position A must possess an energy $E_A$ to push the host atoms away and move into the neighboring void at B.


**Fig. 1.29**
After N jumps, the impurity atom would have been displaced from the original position at O.

Fig. 1.30: An impurity atom has four site choices for diffusion to a neighboring interstitial vacancy. After N jumps, the impurity atom would have been displaced from the original position at O.

The crystal structure of copper is Face Centered Cubic (FCC). The atoms are positioned at well-defined sites arranged periodically and there is a long range order in the crystal. (b) An FCC unit cell with closed-packed hard spheres representing the Fe atoms. (c) Reduced sphere representation of the FCC unit cell. Examples: Ag, Al, Au, Ca, Cu, Fe (>912°C), Ni, Pd, Pt, Rh, Rh.
HCP Structures


Examples: Be, Mg, α-Ti (< 882°C), Cr, Co, Zn, Zr, Cd
Special Structures of Materials CsCl type

Examples: Alkali metals (Li, Na, K, Rb), Cr, Mo, W, Mn, $\alpha$-Fe ($< 912^\circ$C), $\beta$-Ti ($> 882^\circ$C).

Fig. 1.34: Body centered cubic (BCC) crystal structure. (a) A BCC unit cell with closely packed hard spheres representing the Fe atoms. (b) A reduced-sphere unit cell.
Fig. 1.35  The diamond unit cell is cubic. The cell has eight atoms. Grey Sn (-Sn) and the elemental semiconductors Ge and Si have this crystal structure.

The diamond unit cell is cubic. The cell has eight atoms. Grey Sn (α-Sn) and the elemental semiconductors Ge and Si have this crystal structure.

Comparison of Diamond and ZnS (GaAs) Type Structures

Structure of Common Semi-conducting Compounds

Single Component - Si or C(Diamond)

Two Component - GaAs

Fig. 1.34: The diamond unit cell is cubic. The cell has eight atoms. Grey Sn (α-Sn) and the elemental semiconductors Ge and Si have this crystal structure.

Fig. 1.36: The Zinc blende (ZnS) cubic crystal structure. Many important compound crystals have the zinc blende structure. Examples: AlAs, GaAs, GaP, GaSb, InAs, InP, InSb, ZnS, ZnTe.

ELECTRONIC MATERIALS
CHAPTER 1
Elementary Materials Science Concept

MSE 433 and Graduate Class Presentation
Spring Semester
February 8, 2005
(After Chapter III Lectures By Dr. Raja Chellappa)

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1.7 THE CRystalline STATE
1.8 Packing and CRYSTALLINE DEFECTS AND THEIR SIGNIFICANCE
1.9 SINGLE-CRYSTAL CZOCHRALSKI GROWTH
1.10 GLASSES AND AMORPHOUS SEMICONDUCTORS
1.11 SOLID SOLUTIONS AND TWO-PHASE SOLIDS
A two-dimensional crystal of pennies and quarters

Table 2.1

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<th>Coordination number</th>
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<th>Coordination geometry</th>
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<td>0–2</td>
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<td>$0.155 \leq \frac{r}{R} &lt; 0.225$</td>
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<tr>
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<td>$0.225 \leq \frac{r}{R} &lt; 0.414$</td>
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<tr>
<td>6</td>
<td>$0.414 \leq \frac{r}{R} &lt; 0.732$</td>
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<td>8</td>
<td>$0.732 \leq \frac{r}{R} &lt; 1$</td>
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<tr>
<td>12</td>
<td>1</td>
<td>0–12, 12–20</td>
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</table>

*The geometry on the left is for the hexagonal close-packed (hcp) structure, and the geometry on the right is for the face-centered cubic (fcc) structure. These crystal structures are discussed in Chapter 3.

<table>
<thead>
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<th>Coordination number</th>
<th>Radius ratio, ( r/R )</th>
<th>Coordination geometry</th>
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<td>8</td>
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*The geometry on the left is for the hexagonal close-packed (hcp) structure, and the geometry on the right is for the face-centered cubic (fcc) structure. These crystal structures are discussed in Chapter 3.*

**Table 2.1**

*Coordination Numbers for Ionic Bonding.*
Fig. 1.37: A possible reduced sphere unit cell for the NaCl (rock salt) crystal. An alternative unit cell may have Na\(^+\) and Cl\(^-\) interchanged. Examples: AgCl, CaO, CsF, LiF, LiCl, NaF, NaCl, KF, KCl, MgO


Fig. 1.38: A possible reduced sphere unit cell for the CsCl crystal. An alternative unit cell may have Cs\(^+\) and Cl\(^-\) interchanged. Examples: CsCl, CsBr, CsI, TlCl, TlBr, TlI.

**Relationship Between the Lattice Parameter and Radius of Atoms and Miller Indices**

Fig. 1.38: The FCC unit cell. The atomic radius is \( R \) and the lattice parameter is \( a \).

Fig. 1.39: The FCC unit cell. The atomic radius is \( R \) and the lattice parameter is \( a \).

Fig. 1.40: (a) A parallelepiped is chosen to describe the geometry of a unit cell. We line the \( x, y, \) and \( z \) axes with the edges of the parallelepiped taking the lower-left rear corner as the origin. (b) Identification of a direction in a crystal. (c) Directions in a cubic crystal system.
Miller Indices \((hk\ell)\):
\[
\frac{1}{2} \quad \frac{1}{2} \quad \infty \rightarrow (210)
\]

(a) Identification of a plane in a crystal

(b) Various planes in the cubic lattice

Fig. 1.41: Labelling of crystal planes and typical examples in the cubic lattice
Fig. 1.41: The (012) plane and planar concentrations in an FCC crystal.

Fig. 1.42 The (012) plane and planar concentrations in an FCC crystal.
Nanotubes is missing in this picture; pl. see your MSE 250 notes.

Actually there are 4 allotropes.
Vacancy Creation and Diffusion

(a) Perfect crystal without vacancies

(b) An energetic atom at the surface breaks bonds and jumps on to a new adjoining position on the surface. This leaves behind a vacancy.

(c) An atom in the bulk diffuses to fill the vacancy thereby displacing the vacancy towards the bulk.

(d) Atomic diffusions cause the vacancy to diffuse into the bulk.

Fig. 1.44 Generation of a vacancy by the diffusion of an atom to the surface and the subsequent diffusion of the vacancy into the bulk.

Point Defects

(a) A vacancy in the crystal. (b) A substitutional impurity in the crystal. The impurity atom is larger than the host atom.

(c) A substitutional impurity in the crystal. The impurity atom is smaller than the host atom.

(d) An interstitial impurity in the crystal. It occupies an empty space between host atoms.

Fig. 1.45: Point defects in the crystal structure. The regions around the point defect become distorted; the lattice becomes strained.

(a) Schottky and Frenkel defects in an ionic crystal.

(b) Two possible imperfections caused by ionized substitutional impurity atoms in an ionic crystal.

Fig. 1.46: Point defects in ionic crystals

Line Defects - Dislocation

(a) Dislocation is a line defect. The dislocation shown runs into the paper.

(b) Around the dislocation there is a strain field as the atomic bonds have been compressed above and stretched below the islocation line.

Fig. 1.46: Dislocation in a crystal is a line defect which is accompanied by lattice distortion and hence a lattice strain around it.


(a) A screw dislocation in a crystal.

(b) The screw dislocation in (a) as viewed from above.

Fig. 1.47: A screw dislocation involves shearing one portion of a perfect crystal with respect to another portion on one side of a line (AB).

Fig. 1.48
Dislocation Lines Connecting Edge and Screw Dislocations

Fig. 1.49: Screw dislocation aids crystal growth because the newly arriving atom can attach to two or three atoms instead of one atom and thereby form more bonds.

Growth spiral on the surface of a polypropylene crystal due to screw dislocation aided crystal growth. (SOURCE: Photo by Phillip Geil, Courtesy of Case Western Reserve University.)

Crystal Growth Initiated by Screw Dislocation Motion

Polycrystalline Diamond Thin Film Structure on Si Substrate
Fig. 1.50: Solidification of a polycrystalline solid from the melt. (a) Nucleation. (b) Growth. (c) The solidified polycrystalline solid. For simplicity, cubes represent atoms.

Fig. 1.51: The grain boundaries have broken bonds, voids, vacancies, strained bonds and "interstitial" type atoms. The structure of the grain boundary is disordered and the atoms in the grain boundaries have higher energies than those within the grains.
At the surface of a hypothetical two-dimensional crystal, the atoms cannot fulfill their bonding requirements and therefore have broken, or dangling, bonds. Some of the surface atoms bond with each other; the surface becomes reconstructed. The surface can have physisorbed and chemisorbed atoms.

Fig. 1.53: Typically a crystal surface has many types of imperfections such as steps, ledges, kinks, crevices, holes and dislocations.

(a) Stoichiometric ZnO crystal with equal number of anions and cations and no free electrons.

(b) Non-Stoichiometric ZnO crystal with excess Zn in interstitial sites as Zn\(^{2+}\) cations.

Fig. 1.54: Stoichiometry and nonstoichiometry and the resulting defect structure.

Czochralski Method of Si Crystal Ingot Production

(a) The schematic illustration of the growth of a single crystal Si ingot by the Czochralski technique. (b) The crystallographic orientation of the silicon ingot is marked by grounding a flat. The ingot can be as long as 2 m. Wafers are cut using a rotating annular diamond saw. Typical wafer thickness is 0.6-0.7 mm.
Czochralski Method Growing a Single crystal of Si For Chip making

Figure 3.22.2

Figure 3.22.1
Courtesy of SEMATECH.
Silicon (or Arsenic) atom
Oxygen (or Selenium) atom

(a) A crystalline solid reminiscent to crystalline SiO$_2$ (Density = 2.6 g cm$^{-3}$)
(b) An amorphous solid reminiscent to vitreous silica (SiO$_2$) cooled from the melt (Density = 2.2 g cm$^{-3}$)

Fig. 1.56: Crystalline and amorphous structures illustrated schematically in two dimensions.
Melt spinning involves squirting a jet of molten metal onto a rotating cool metal drum. The molten jet is instantly solidified into a glassy metal ribbon which is a few microns in thickness. The process produces roughly one to two kilometers of ribbon per minute.

SOURCE: Photo courtesy of the Estate of Fritz Goro.

Fig. 1.57: It is possible to rapidly quench a molten metallic alloy and thereby bypass crystallization and form a glassy metal commonly called a metallic glass. The process is called melt spinning.
Fig. 1.58: Silicon can be grown as a semiconductor crystal or as an amorphous semiconductor film. Each line represents an electron in a bond. A full covalent bond has two lines and a broken bond has one line.

Amorphous and Hydrogenated Si Production

Fig. 1.59: Amorphous silicon, a-Si, can be prepared by an electron beam evaporation of silicon. Silicon has a high melting temperature so that an energetic electron beam is used to melt the crystal in the crucible locally and thereby vaporize Si atoms. Si atoms condense on a substrate placed above the crucible to form a film of a-Si.


Fig. 1.60: Hydrogenated amorphous silicon, a-Si:H, is generally prepared by the decomposition of silane molecules in a radio frequency (RF) plasma discharge. Si and H atoms condense on a substrate to form a film of a-Si:H.

Solid Solutions – Order- Disorder

(a) Disordered Substitutional Solid Solution. Example: Cu-Ni alloys ({100} planes)

(b) Ordered Substitutional Solid Solution. Example: Cu-Zn alloy of composition 50%Cu-50%Zn. ({110} planes).

(c) Interstitial Solid Solution. Example: Small number of C atoms in FCC Fe (austenite). ({100} planes)

Fig. 1.61: Solid solutions can be disordered substitutional, ordered substitutional and interstitial substitutional. There is only one phase within the alloy which has the same composition, structure and properties everywhere.
Phase Diagrams and Equilibrium Cooling

Fig. 1.62: Solidification of an isomorphous alloy such as Cu-Ni. (a) Typical cooling curves. (b) The phase diagram marking the regions of existence for the phases.

Fig. 1.63: Cooling of a 80%Cu-20%Ni alloy from the melt to the solid state.

Phase Diagrams and Non-equilibrium Cooling

Low Level Solid Solution and Segregation Due to Rapid Cooling

Fig. 1.65: The phase diagram of Si with impurities near the low concentration region.

01/24/2006 Electronic Materials D. Chandra
(a) Heat is applied locally starting at one end. The impurity concentration in the re-frozen solid at B is $C_B < C_0$. The impurity concentration in the melt is $C_{L'} > C_0$.

(b) As the torch travels towards the right, the refrozen solid at B' has $C_B'$, where $C_B < C_B' < C_0$. The impurity concentration in the melt is now even greater than $C_{L'}$.

(c) The impurity concentration profile in the refrozen solid after one pass.

(d) Typical impurity concentration profile after many passes.

**Fig. 1.66: The principle of zone refining**

Fig. 1.67: We can only dissolve so much salt in brine (solution of salt in water). Eventually we reach the solubility limit at $X_s$ which depends on the temperature. If we add more salt than the excess salt does not dissolve and coexists with the brine. Past $X_s$ we have two phases, brine (solution) and salt (solid).


Fig. 1.68: The equilibrium phase diagram of the Pb-Sn alloy. The microstructures on the left show the observations at various points during the cooling of a 90% Pb-10% Sn from the melt along the dashed line (the overall alloy composition remains constant at 10% Sn).

Fig. 1.69: The alloy with the eutectic composition cools like a pure element exhibiting a single solidification temperature at 183°C. The solid has the special eutectic structure. The alloy with the composition 60% Pb-40% Sn when solidified is a mixture of primary and eutectic solid.

Fig. 1.70: (a) A simple square lattice. The unit cell is a square with a side $a$. (b) Basis has two atoms. (c) Crystal = Lattice + Basis. The unit cell is a simple square with two atoms. (d) Placement of basis atoms in the crystal unit cell.
Fig. 1.71: The seven crystal systems (unit cell geometries) and fourteen Bravais lattices.

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