Materials are critical nation's quality of life, security and economic strength.

- building blocks for advanced technologies
- tools for addressing urgent problems, such as pollution, declining natural resources and escalating costs.

"materials are like people; it is the defects that make them interesting"

Materials science or **materials engineering** is an interdisciplinary field involving the properties of matter and its applications to various areas of science and engineering.

This science investigates the relationship between the structure of materials and their properties. It includes elements of applied physics and chemistry, as well as chemical, mechanical, civil and electrical engineering. With significant media attention to nanoscience and nanotechnology especially nowadays.

The material of choice of a given era is often its defining point:

1. Stone age
2. Bronze Age
3. Steel age

Materials size scale

~ 0.1×10^{-9} m or 0.1 nm → **atomic scale**
~ 50×10^{-6} m or 50 µm → **microscopic scale**
~ 10^{-2} m or 1 cm → **macroscopic scale**

Fundamentals of Materials

1. **Molecule** – is the smallest particle of a compound that retains all the characteristics of the compound.

2. **Atom** – is the smallest particle of an element that retains all the characteristics of that element.

3. **Compound** – a chemical combination of two or more elements that can be separated by chemical means, but not by physical means.

4. **Element** – substance that cannot be reduced to a simpler substance by chemical means.

Atomic Structure

Proton – positively charge particle
the charge on the proton is equal to 1.6 X 10 – 19 Coulomb
mass of 1.67 X 10 -27 Kg
The total number of protons gives the Atomic Number of the element

Electron – negatively charge particle
the charge on the electron is equal to 1.6 X 10 – 19 Coulomb
mass of 9.1 X 10 -31 Kg

Neutron – neutral particle
Mass of 1.675 X 10 -27 Kg

Valence electrons – the number of electrons in the outermost shell (valence shell) that determine the valence of an atom.

Intrinsic material – pure (Si or Ge)

Extrinsic material – impure
Doping – adding of impurities to semiconductor devices

Two types of extrinsic

1. n-type
2. p-type

N-type

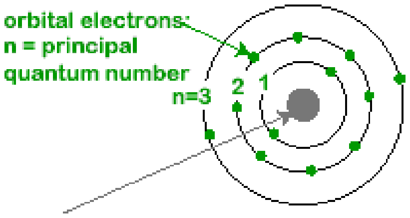
To increase the number of conduction band electrons in intrinsic material, impurity atoms are added (Pentavalent)
These atoms with five valence electrons (Ar, P, Bi and Sb)
pentavalent – donor atom
Holes in n-type are called minority carriers

P-type

To increase the number of holes in intrinsic material, impurity atoms are added (trivalent)
These atoms with three valence electrons (B, In, Al and Ga)
Trivalent - acceptor
Electrons in p-type are called minority carriers

Atomic Model

BOHR ATOM



Nucleus: Z = # protons
= 1 for hydrogen to 94 for plutonium
N = # neutrons

Atomic mass A = Z + N

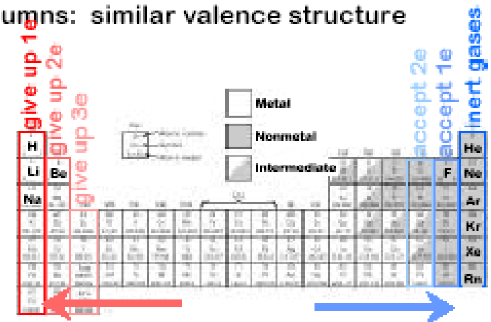
Most elements: Electron configuration not stable

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)

Why? Valence (outer) shell usually not filled

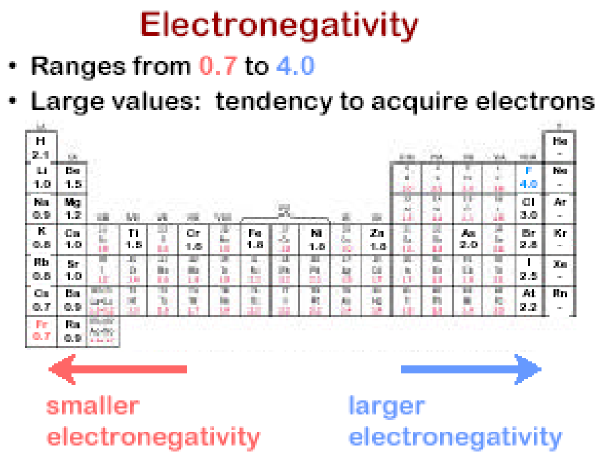
The Periodic Table

Columns: similar valence structure



Electropositive elements: readily give up electrons (+ ions)

Electronegative elements: readily accept electrons (- ions)



Electronegativity

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

smaller electronegativity

larger electronegativity

$$\text{Mass of an element} = \frac{\text{Number of atom/s X Atomic Mass}}{\text{Avogadro's Number}}$$

Avogadro's Number = 6.023 X 10^{23} atoms/mole

Problem
What is the mass in grams of one atom of copper?

Ans: 1.05 X 10^{-22} gram

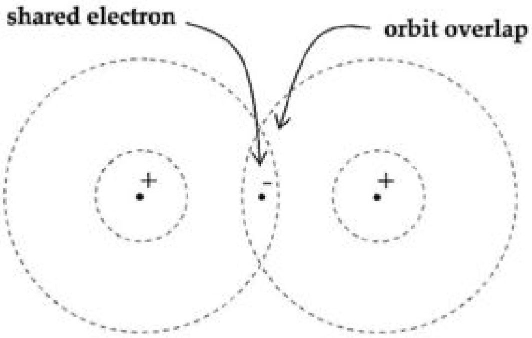
Problem
How many copper atoms are in 1 gram of copper?

Ans: 9.47 X 10^{21} atoms

Chemical Bonding

A **chemical bond** is the physical process responsible for the attractive interactions between atoms and molecules, and that which confers stability to diatomic and polyatomic chemical compounds.

Molecules, crystals, and diatomic gases—indeed most of the physical environment around us—are held together by chemical bonds, which dictate the structure of matter.



Lewis-type Chemical bond

Six rules for the shared electron bond:

1. The electron-pair bond forms through the interaction of an unpaired electron on each of two atoms.
2. The spins of the electrons have to be opposed.
3. Once paired, the two electrons cannot take part in additional bonds.
4. The electron-exchange terms for the bond involve only one wave function from each atom.
5. The available electrons in the lowest energy level form the strongest bonds.
6. Of two orbitals in an atom, the one that can overlap the most with an orbital from another atom will form the strongest bond, and this bond will tend to lie in the direction of the concentrated orbital.

Chemical Bond

A. Primary Bonds (Stronger)

1. Covalent Bonding
   Polar covalent bonding is intermediate in character between a covalent and an ionic bond.
2. Ionic Bonding
3. Metallic Bonding

B. Secondary Bonds (Weak) - Intermolecular Bonding

1. Permanent dipole to permanent dipole
2. Hydrogen Bond
3. Instantaneous to induced dipole (van der Waals)
4. Cation-pi reaction

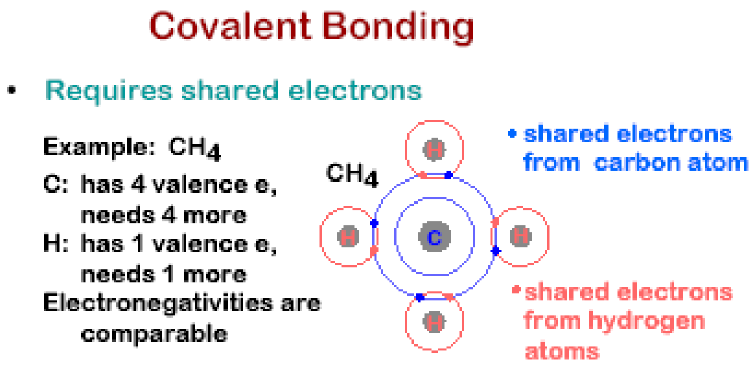
A. Primary Bonding

Covalent Bonding – one or more electrons are drawn into the space between the two atomic nuclei. Here the negatively charged electrons are attracted to the positive charges of *both* nuclei, instead of just their own. **Bonds within most organic compounds.**

Covalent bonding is a common type of bonding, in which the electronegativity difference between the bonded atoms is small or non-existent.

Covalent bonding involves sharing of electrons in which the positively charged nuclei of two or more atoms simultaneously attract the negatively charged electrons that are being shared.

This overcomes the repulsion between the two positively charged nuclei of the two atoms and so this overwhelming attraction holds the two nuclei in a relatively fixed configuration of equilibrium, even though they will still vibrate at equilibrium position.



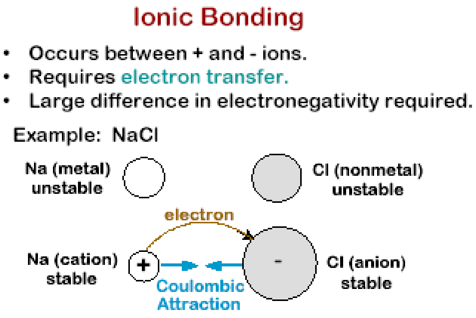
Covalent Bonding

- Requires shared electrons

Example: CH_4
C: has 4 valence e,
needs 4 more
H: has 1 valence e,
needs 1 more
Electronegativities are
comparable

Ionic Bonding (electrovalent bond) - is a type of electrostatic interaction between atoms which have an electronegativity. The chemical bond based on electrostatic forces between two oppositely-charged ions. In ionic bond formation, a metal donates an electron, due to a low electronegativity, to form a positive ion or cation.

Ex. NaCl



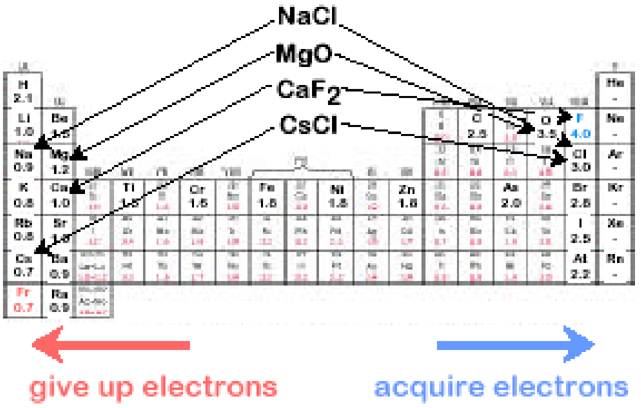
Ionic Bonding

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

Example: NaCl

Examples: Ionic Bonding

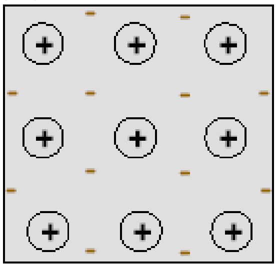
- Predominant bonding in ceramics



Metallic Bonding - bonding electrons are delocalized over a lattice of atoms. Solids composed primarily of electropositive elements containing three or fewer valence electrons held by together by this bond.

Metallic Bonding

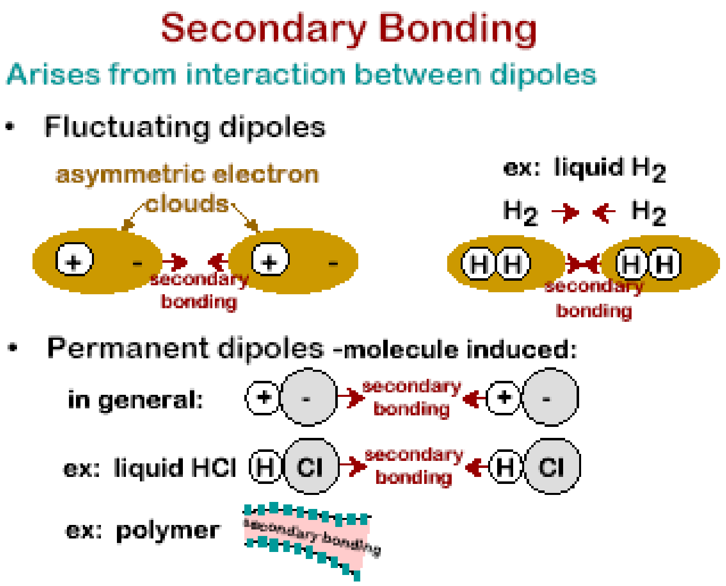
- Arises from sea of donated valence electrons (1, 2, or 3 from each atom)



- Primary bond for metals and their alloys

B. Secondary Bonding

There are four basic types of bonds that can be formed between two or more molecules, ions or atoms. Intermolecular forces cause molecules to be attracted or repulsed by each other. Often, these define some of the physical characteristics (such as the melting point) of a substance.



Secondary Bonding

Arises from interaction between dipoles

- Fluctuating dipoles

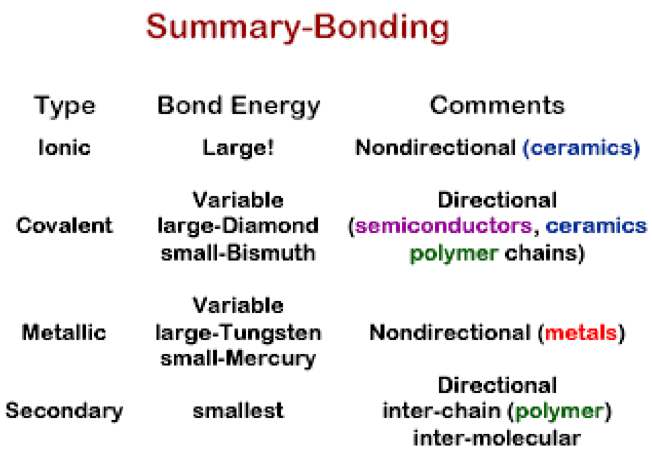
- Permanent dipoles -molecule induced:

Permanent dipole to permanent dipole - A large electronegativity difference between two strongly bonded atoms within a molecule causes a dipole to form (a dipole is a pair of permanent partial charges). Dipoles will attract or repel each other.

Hydrogen bond - In the hydrogen bond, the hydrogen proton comes closer to being shared between target and donor atoms, in a three-center two-electron bond like that in diborane. Hydrogen bonds explain the relatively high boiling points of liquids like water, ammonia, and hydrogen fluoride.

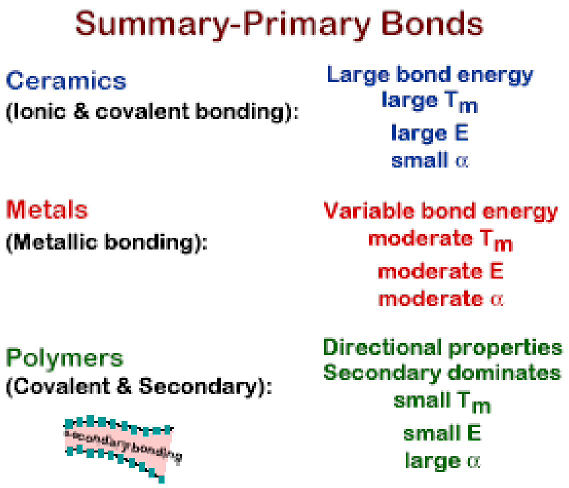
Instantaneous dipole to induced dipole (van der Waals) - Instantaneous dipole to induced dipole, or van der Waals forces, are the weakest, but also the most prolific/versatile—occurring between all chemical substances. Imagine a helium atom: At any one point in time, the electron cloud around the (otherwise neutral) atom can be thought to be slightly imbalanced, with momentarily more negative charge on one side. This is referred to as an instantaneous dipole. This dipole, with its slight charge imbalance, may attract or repel the electrons within a neighboring helium atom, setting up another dipole. The two atoms will be attracted for an instant, before the charge rebalances and the atoms move on.

Cation-pi interaction - occur between the localized negative charge of π orbital electrons, located above and below the plane of an aromatic ring, and a positive charge.



Summary-Bonding

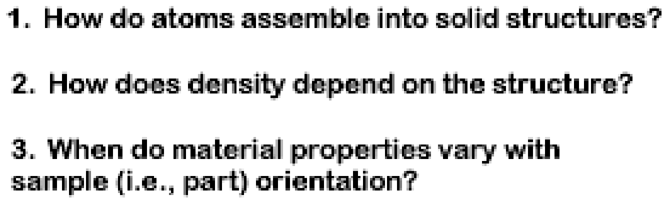
Type	Bond Energy	Comments
Ionic	Large!	Nondirectional (ceramics)
Covalent	Variable large-Diamond small-Bismuth	Directional (semiconductors, ceramics polymer chains)
Metallic	Variable large-Tungsten small-Mercury	Nondirectional (metals)
Secondary	smallest	Directional inter-chain (polymer) inter-molecular



Summary-Primary 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 dominates small T_m small E large α

Crystal Lattice Structure



1. How do atoms assemble into solid structures?
2. How does density depend on the structure?
3. When do material properties vary with sample (i.e., part) orientation?

A **crystal structure** is a unique arrangement of atoms in a crystal.

A crystal structure is composed of a **motif**, a set of atoms arranged in a particular way, and a lattice.

Motifs are located upon the points of a lattice, which is an array of points repeating periodically in three dimensions.

A **lattice** is a regular array of lattice points in three dimensions, and a **crystallographic unit cell** is a parallelepiped formed by connecting eight lattice points.

The **points** can be thought of as forming identical tiny boxes, called unit cells, that fill the space of the lattice.

The lengths of the edges of a unit cell and the angles between them are called the **lattice parameters.**

The units cells **stacked** in three-dimensional space describes the bulk arrangement of atoms of the crystal.

The symmetry properties of the crystal are embodied in its space group.

A crystal's structure and symmetry play a role in determining many of its properties.

A **cubic** unit cell is characterized by six square faces and three equal non-coplanar edges:
$a = b = c$. The volume of a cubic unit cell is $a \cdot b \cdot c$ or

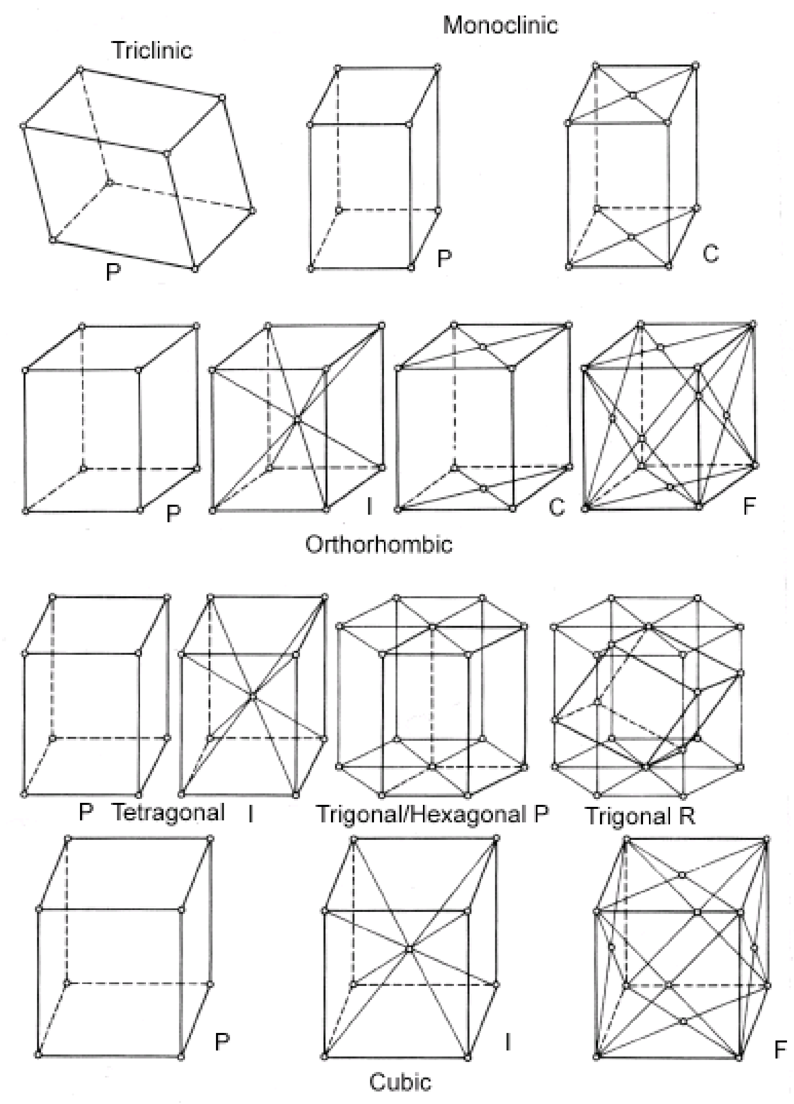
$$\mathbf{V = a^3}$$

A **hexagonal** unit cell is characterized by four rectangular faces (with edges a & c and b & c) and two parallelograms with equal sides ($a = b$) and interior angles of 60^o and 120^o. The volume of a hexagonal unit cell is $a \cdot b \cdot c \cdot \sin(120^o)$ or

$$V = \frac{\sqrt{3}}{2} a^2 c$$

Bravais Lattice

Bravais lattice, when the crystal systems are combined with the various possible lattice centering. They describe the geometric arrangement of the lattice points, and thereby the translational symmetry of the crystal. In three dimensions, there are **14 unique** Bravais lattices which are distinct from one another in the translational symmetry they contain. The Bravais lattices are sometimes referred to as **space lattices**.



Coordination Number (CN). Numbers of the nearest neighbor atom.

Density

THEORETICAL DENSITY, ρ

atoms/unit cell

Atomic weight (g/mol)

$$\rho = \frac{nA}{V_c N_A}$$

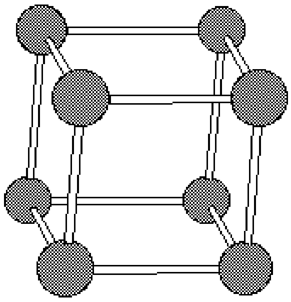
(units = mass/volume)

Volume/unit cell
(cm^3/unit cell)

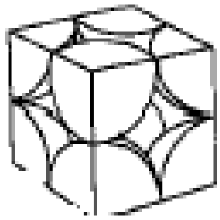
Avogadro's number
(6.023 X 10^{23} atoms/mol)

Basic Crystal Structures

1. Simple Cubic (SC) unit cell there is one lattice point at each of the eight corners of a cube. Unit cells in which there are lattice points only at the eight corners are called **primitive**



1 unit cell

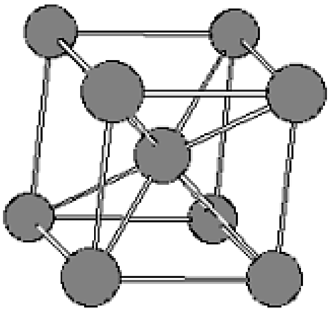


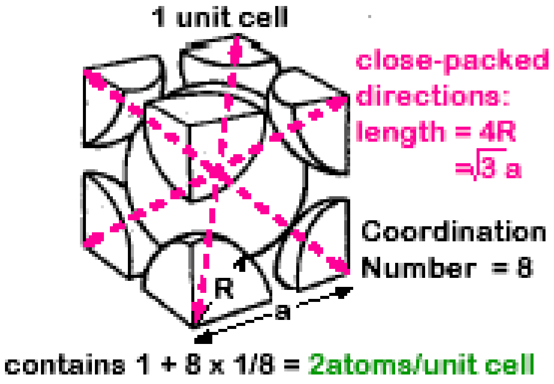
(contains 8 x 1/8 = 1 atom)

There is one atom wholly inside the cube (Z = 1)

CN = 6

2. **Body Centered Cubic (BCC)** - There is one host atom at each corner of the cubic unit cell and one atom in the cell center. Each atom touches eight other host atoms along the body diagonal of the cube (a = 2.3094r, Z = 2).





Problem

Calculate the density if the BCC iron, having the following characteristics:

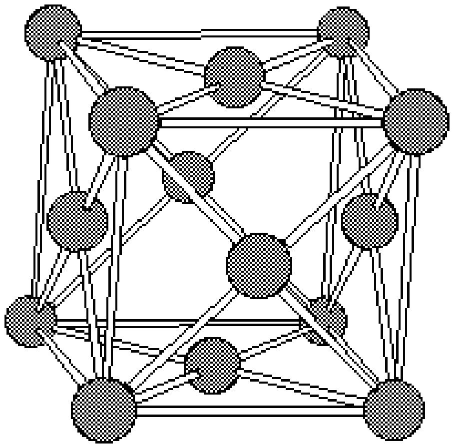
Fe atomic mass: 55.85 g/mol

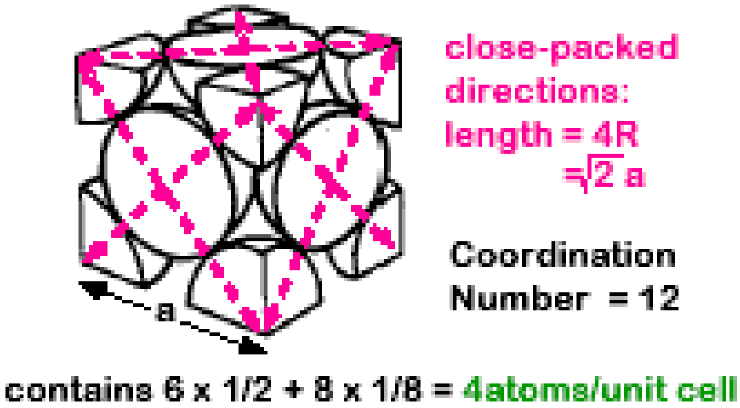
Fe atomic radius: 1.24 X 10^{-8} cm

Ans: 7.87 g/cm^3

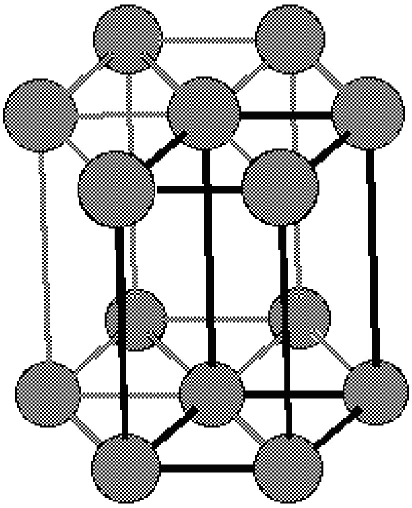
3. Face Centered Cubic (FCC) - There is one host atom at each corner, one host atom in each face, and the host atoms touch along the face diagonal (a = 2.8284r, Z = 4).

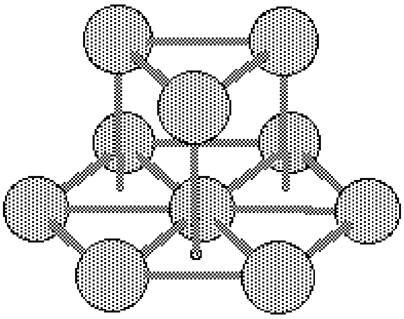
This lattice is "closest packed", because spheres of equal size occupy the maximum amount of space; since this closest packing is based on a cubic array, it is called "**cubic closest packing**": CCP = FCC.

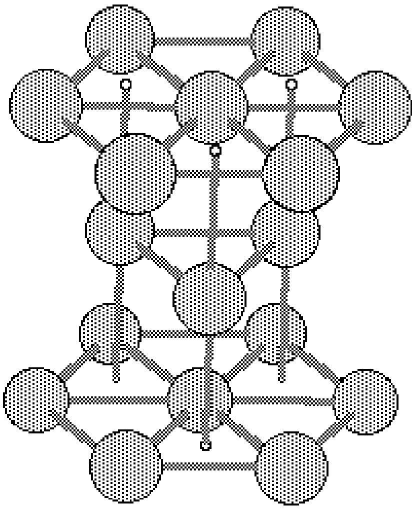


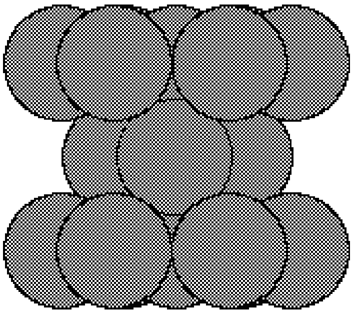


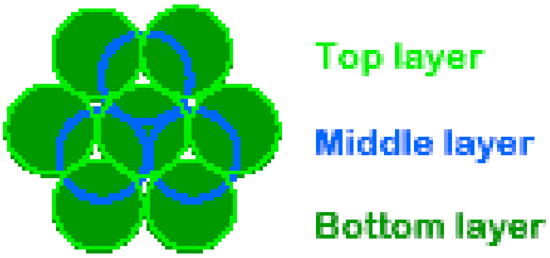
4. Hexagonal Closest Packing (HCP) - To form a three-dimensional closest packed structure, the hexagonal closest packed planes must be stacked such that atoms in successive planes nestle in the triangular "grooves" of the preceding plane. Note that there are six of these "grooves" surrounding each atom in the hexagonal plane, but only three of them can be covered by atoms in the adjacent plane.











Packing Efficiency/Atomic Packing Factor (APF)
The **packing efficiency** of a lattice is defined as the ratio $\mathbf{V_s{:}V_c}$

APF = $V_s{:}V_c$

V_s **= volume of a sphere**
$= V_s = {}^{4}/_{3}\pi r^3$

V_c = **volume of the cell**

Problem
Calculate the packing efficiency of the Simple Cubic (SC).

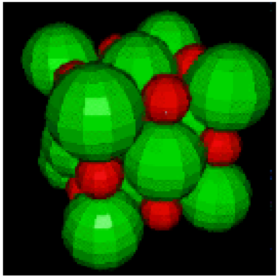
Ans: ~ 52%

BCC = 68%
FCC = 74%
HCP = ~ 60%

Crystal Imperfection

Compounds have Similar Structures
(sometimes more complicated)

example: NaCl



DENSITIES OF MATERIAL CLASSES

$\rho_{\text{metals}} \geq \rho_{\text{ceramics}} \geq \rho_{\text{polymers}}$

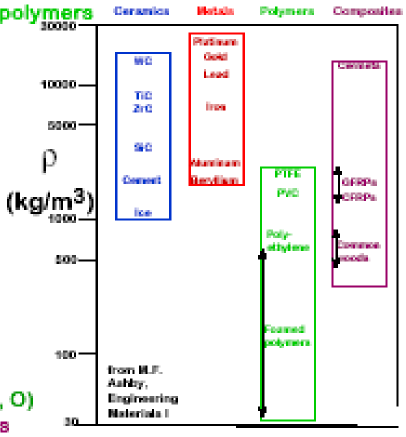
Why?

Metals have...
- close-packing
  (metallic bonding)
- large atomic masses

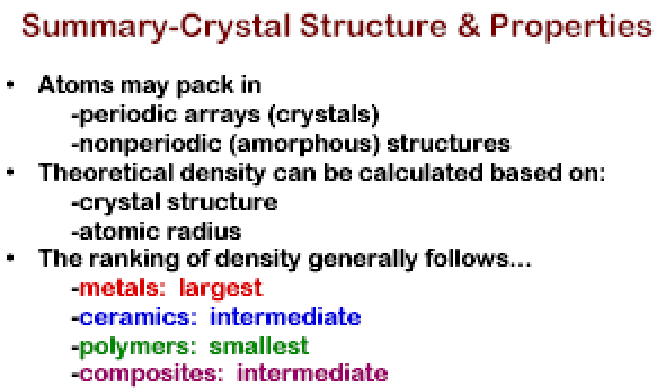
Ceramics have...
- less dense packing
  (covalent bonding)
- often lighter elements
  (oxygen, carbon)

Polymers have...
- poor packing
  (often amorphous)
- lighter elements (C, H, O)

Composites-average values



from M.F. Ashby, Engineering Materials I

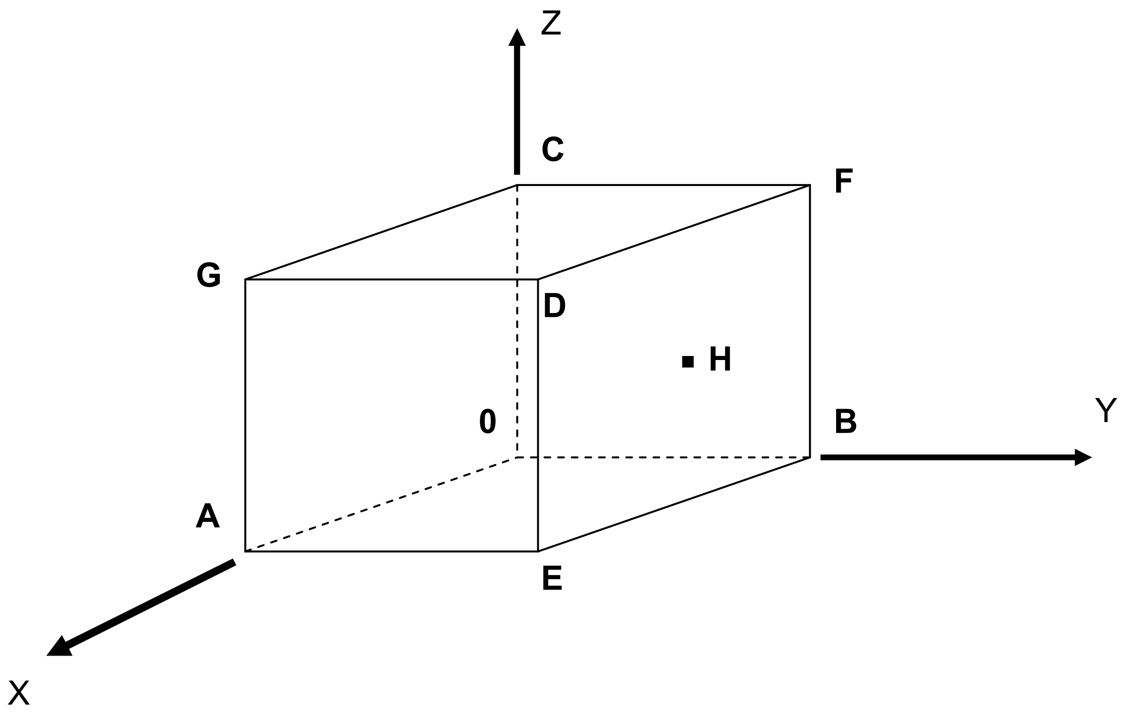


Summary-Crystal Structure & Properties

- Atoms may pack in
  - -periodic arrays (crystals)
  - -nonperiodic (amorphous) structures
- Theoretical density can be calculated based on:
  - -crystal structure
  - -atomic radius
- The ranking of density generally follows...
  - -metals: largest
  - -ceramics: intermediate
  - -polymers: smallest
  - -composites: intermediate

Miller Indices

Coordinates of points based on Cartesian Coordinates



Positions	Coordinates
0	0, 0, 0 (origin)
A	1, 0, 0
B	0, 1, 0
C	0, 0, 1
D	1, 1, 1,
E	1, 1, 0
F	0, 1, 1,
G	1, 0, 1
H	1/2, 1, 1/2

Factors of Crystalline Structures

1. Linear Density ρ_L

= the number of equivalent lattice points per unit length along a direction

$$= \frac{\text{Number of atoms centered along direction within one unit cell}}{\text{Length of the line contained within one unit cell}}$$

atoms/meter

2. Planar Density ρ_P

= the number of atoms per unit area on a plane of interest

$$= \frac{\text{Number of atoms centered on a plane within one unit cell}}{\text{Area of the plane contained within one unit cell}}$$

atoms/m^2

Problem

Calculate the linear density along [1 1 1] in a BCC material.

Ans: 1/(2r)

Problem

Determine the planar density of (1 1 0) in a FCC crystal.

Ans: $\frac{1}{4\sqrt{2}\,r^2}$

Five classes of Materials

1. Metals
2. Ceramics
3. Polymers
4. Composites
5. Semiconductors

Metals

Metal (Greek: *fudgeon*) fudgean element that readily loses electrons to form positive ions (cations) and has metallic bonds between metal atoms. Metals form ionic bonds with non-metals.

The traditional definition focuses on the bulk properties of metals. They tend to be lustrous, ductile, malleable, and good conductors of electricity, while nonmetals are generally brittle, lack luster, and are insulators.

Ceramic

Ceramic materials are inorganic, nonmetallic materials which consist of metallic and nonmetallic elements bonded together primarily by ionic and/or covalent bonds.

Polymers

A **polymer** is a substance composed of molecules with large molecular mass composed of repeating structural units, or monomers, connected by covalent chemical bonds. The word is derived from the Greek, πολυ, polu, "many"; and μέρος, meros, "part"). Well known examples of polymers include plastics, DNA and proteins.

Composites

Composite materials (or **composites** for short) are engineered materials made from two or more constituent materials with significantly different physical or chemical properties and which remain separate and distinct on a macroscopic level within the finished structure.

Semiconductor

A **semiconductor** is a solid that has electrical conductivity in between that of a conductor and that of an insulator, and can be controlled over a wide range, either permanently or dynamically. Semiconductors are tremendously important in technology. Semiconductor devices, electronic components made of semiconductor materials, are essential in modern electrical devices. Examples range from computers to cellular phones to digital audio players. Silicon is used to create most semiconductors commercially, but dozens of other materials are used as well.