Metals and Semi-Conductors

6.4

Unit Cells for

Cubic Close-Packed Spheres

Hexagonal Close-Packed Spheres

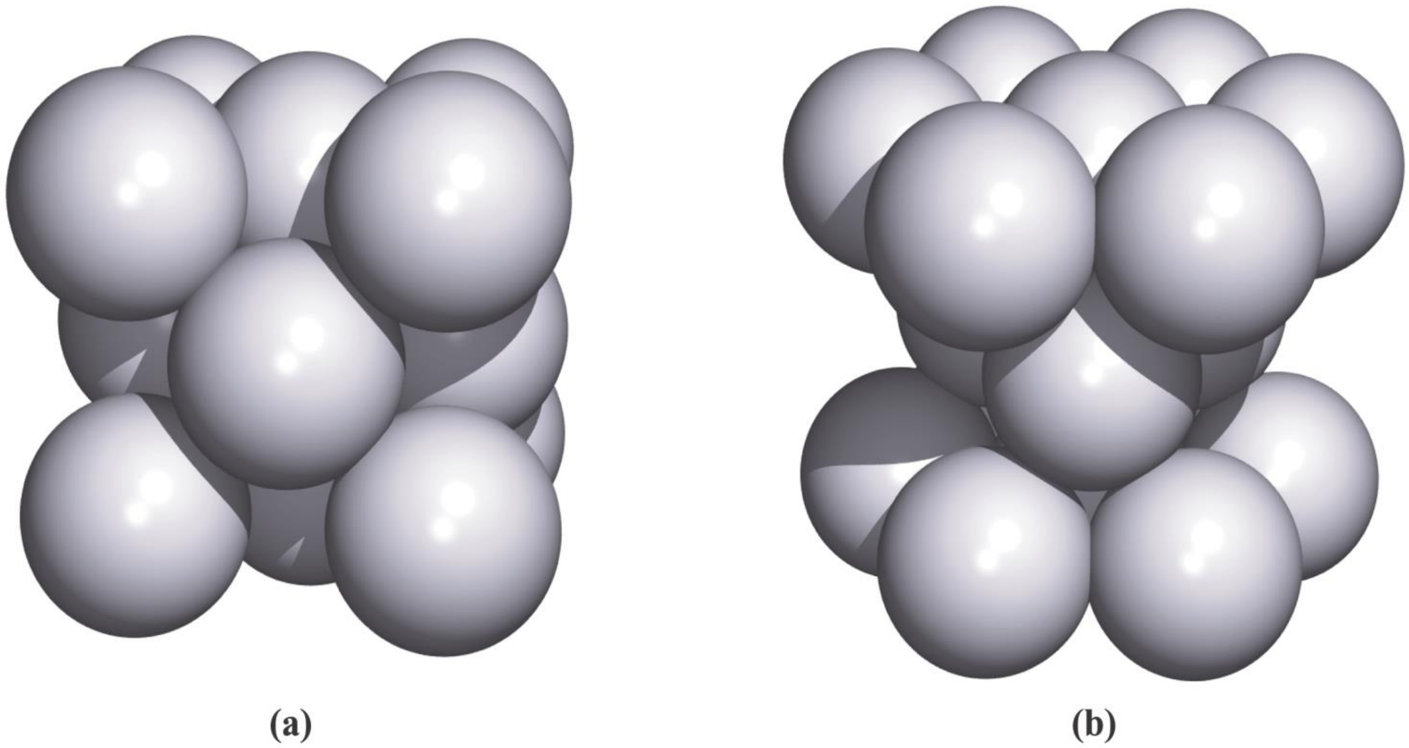


Fig. 6.4 Unit cells of (a) a cubic close-packed (face-centred cubic) lattice and (b) a hexagonal close-packed lattice.

W. H. FREEMAN

Table 3.2 The crystal structures adopted by metals under normal conditions

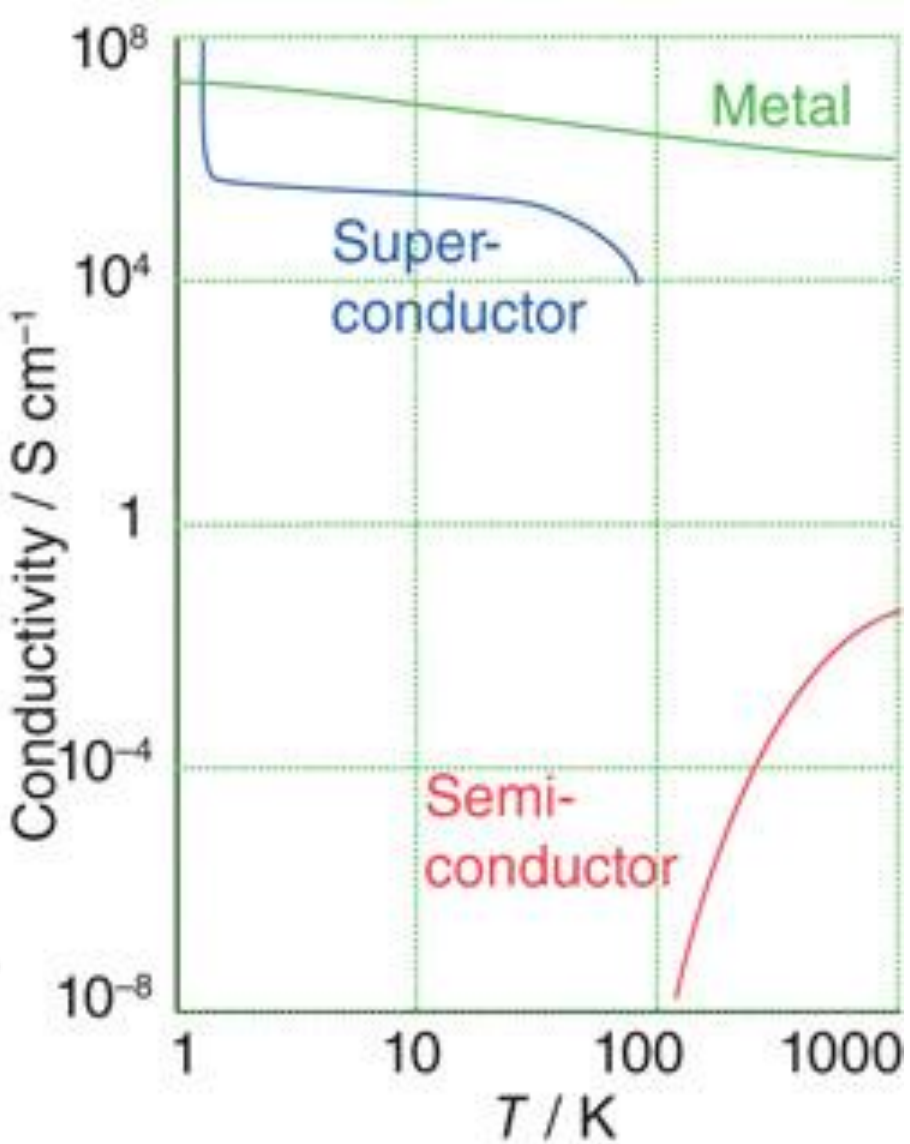
Crystal structure	Element
Hexagonal close-packed (hcp)	Be, Ca, Co, Mg, Ti, Zn
Cubic close-packed (ccp)	Ag, Al, Au, Cd, Cu, Ni, Pb, Pt
Body-centred cubic (bcc)	Ba, Cr, Fe, W, alkali metals
Primitive cubic (cubic-P)	Po

What are the characteristics of the metals that might be correlated with their crystal structures? What is metallic Bonding? Can MO theory describe it? Account for properties?

Metals T ↑ C ↓

Semi- T ↑ C ↑

Conductor



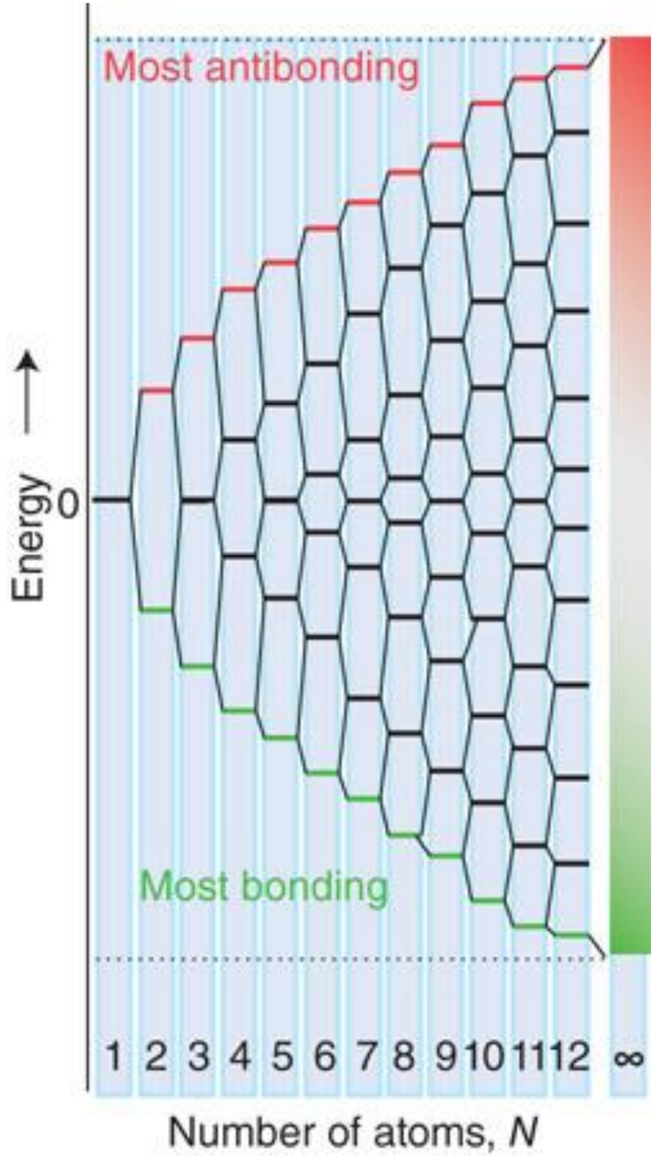
The simple model of M-M interactions in a solid:

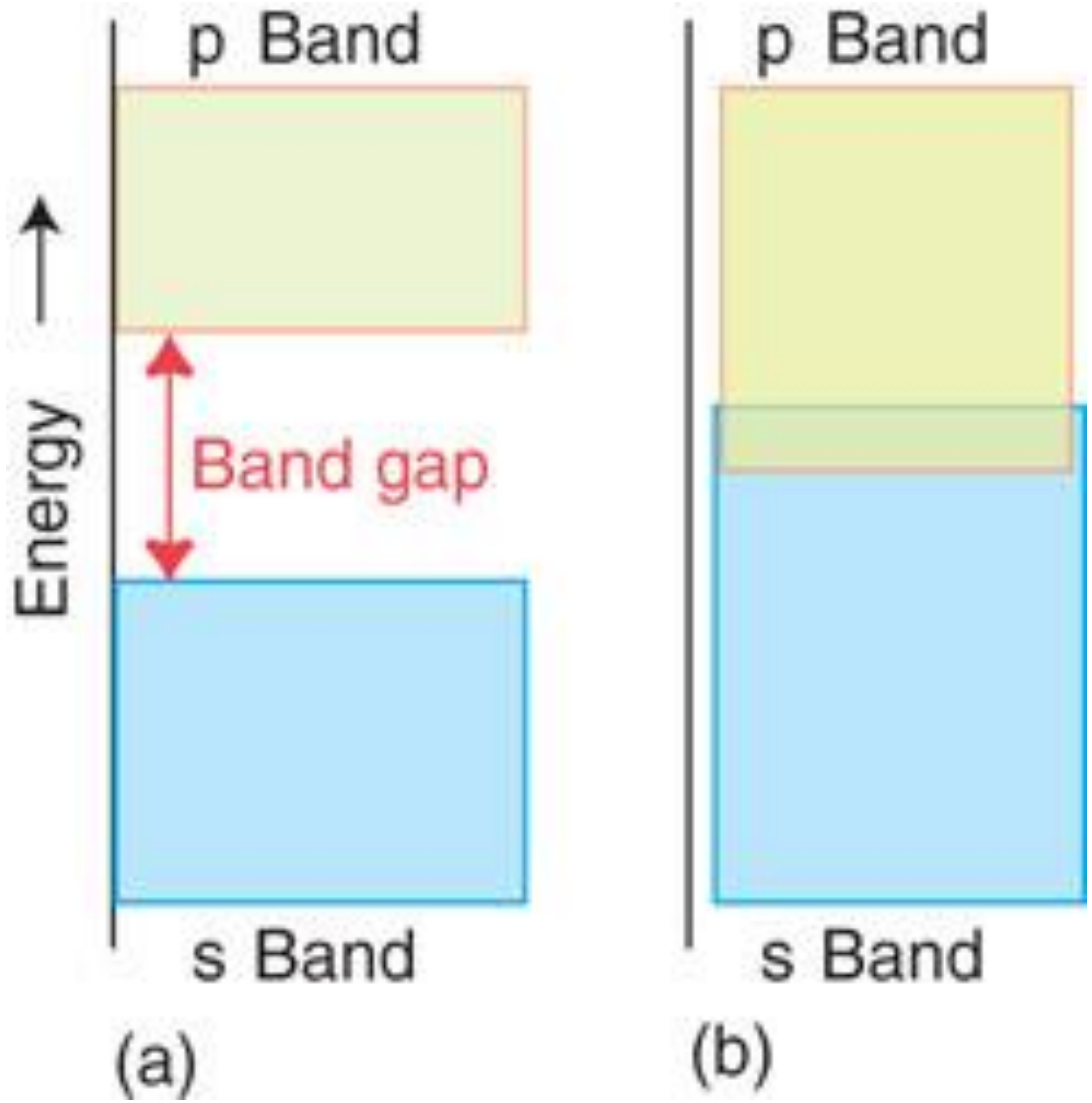
A“sea” of electrons surrounding metal ions

Explains:

Conductivity and Temperature Dependence
Luster
Malleability and Ductility

Advanced model: MO theory


Most antibonding
Most bonding
Energy
0
1 2 3 4 5 6 7 8 9 10 11 12 ∞
Number of atoms, N


p Band
Energy
Band gap
s Band
(a)
p Band
s Band
(b)

6.12

Metals vs. insulators
Vs. semiconductors

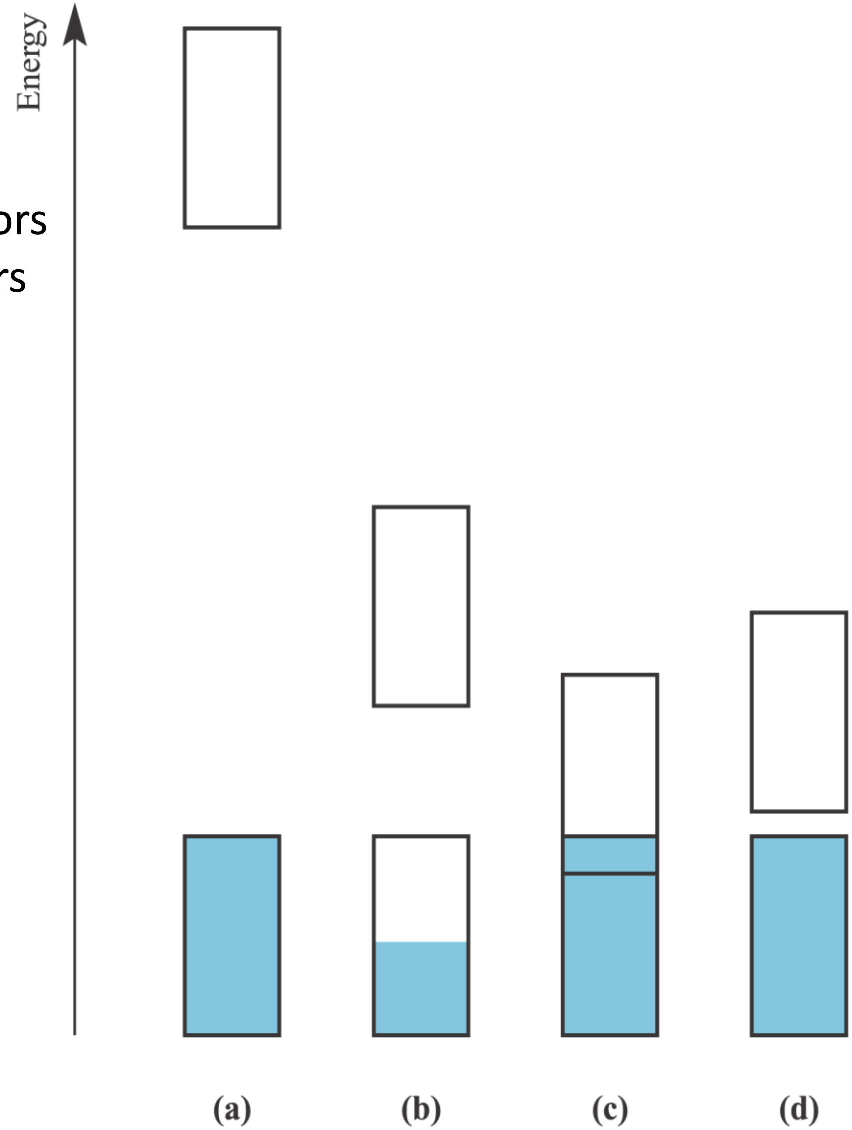
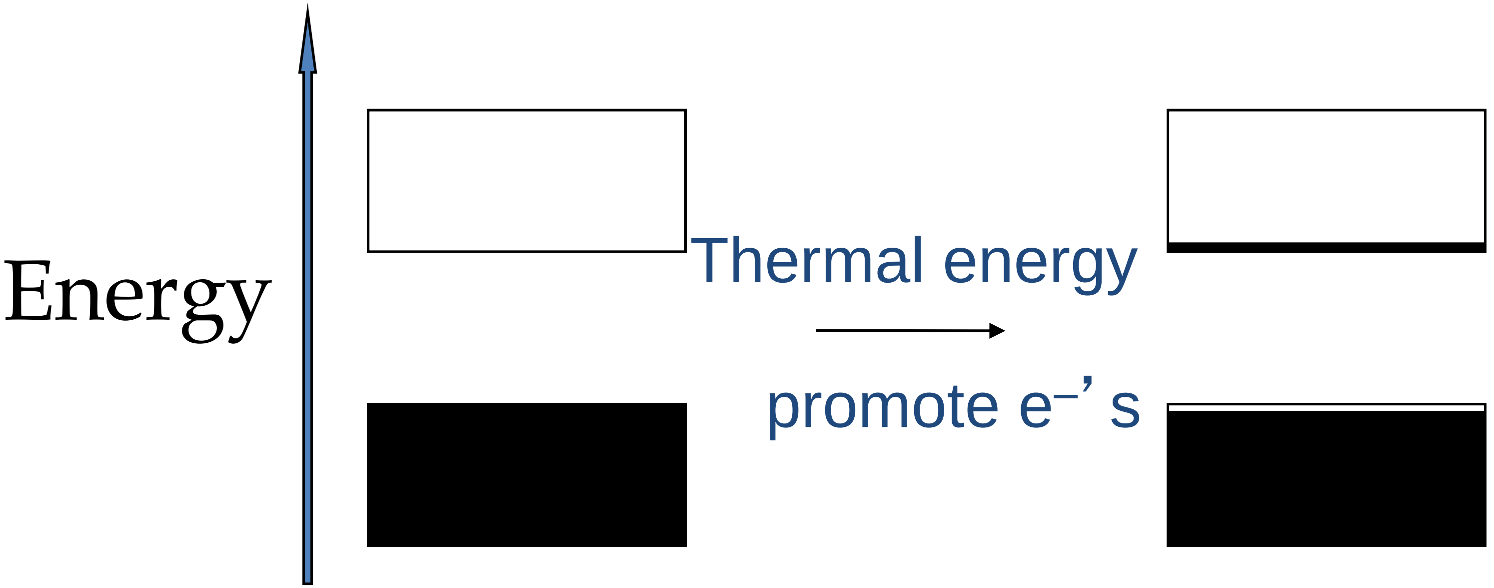


Fig. 6.12 The relative energies of occupied and empty bands in (a) an insulator, (b) a metal in which the lower band is only *partially* occupied, (c) a metal in which the occupied and empty bands overlap and (d) a semiconductor.

Typical Band Gaps

Material	E_g/eV
Carbon (diamond)	5.47
Silicon carbide	3.00
Silicon	1.11
Germaniun	0.66
Gallium arsenide	1.35
Indium arsenide	0.36

Semiconductors



- Energy from heat (thermal equilibrium), gives (virtually Boltzmann-like) distribution of excited states where some electrons are promoted.
- When electrons have been promoted (heat, light), the material will begin to conduct.

Semiconductors

- If the band gap becomes small enough, some conductivity can be achieved.
- Band gaps:

diamond:	580 kJ/mol	(λ ~ 206 nm)
silicon:	105 kJ/mol	(λ ~ 1140 nm)
germanium:	64 kJ/mol	(λ ~ 1870 nm)

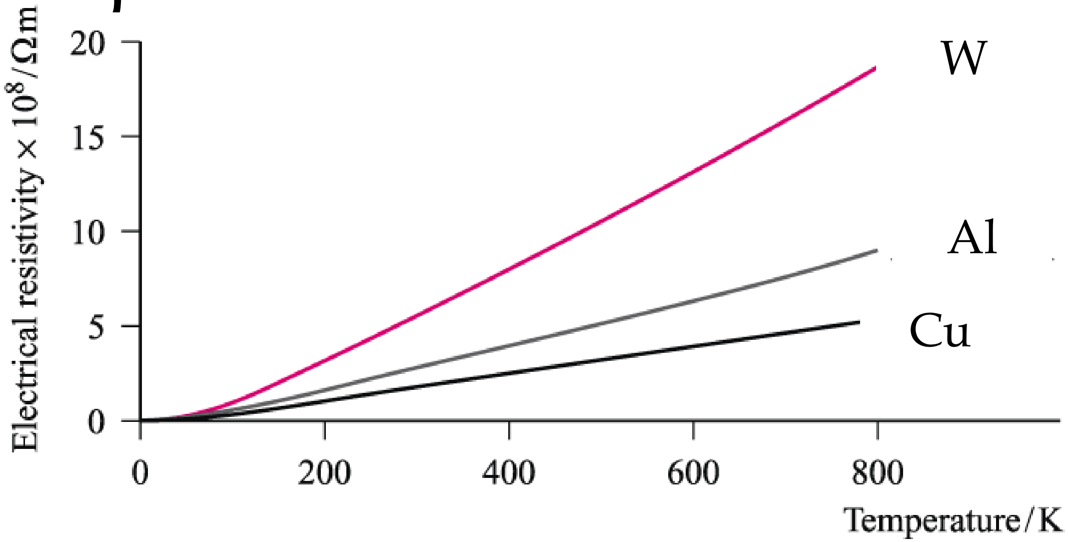
- Pure Si or Ge can conduct at high T or if exposed to light.

https://www.youtube.com/watch?v=kD1O9B5CUUw

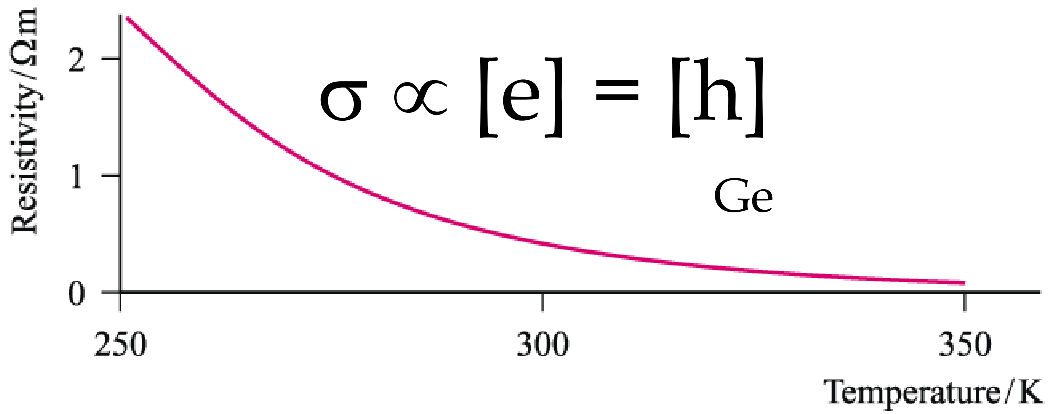
Metals vs Semiconductors

Resistivities = $\rho = 1/\sigma$

- Metals' resistivities increase with T



- Semiconductors' resistivities decrease with T
- However, note the huge difference in scales on these plots!



$$\sigma \propto [e] = [h]$$

"Intrinsic" (pure, undoped) Semiconductors

- Moderate band gaps - conductivity is low but increases with temperature:

$$[e][h] = K_{eq} = e^{-\Delta G^\circ/RT} = (e^{\Delta S^\circ/R})e^{-\Delta H^\circ/RT}$$

$$\Delta H^\circ \approx \Delta E = E_{gap} \qquad \text{also} \quad [e] = [h]$$

$$[e] = [h] \approx (e^{\Delta S^\circ/2R}) \bullet e^{-E_{gap}/2RT}$$

- Conductivity is thus an <u>activated process</u> in a pure semiconductor.

$\Rightarrow$ Plot ln? vs. (1/T) to get slope = $E_{gap}/2$

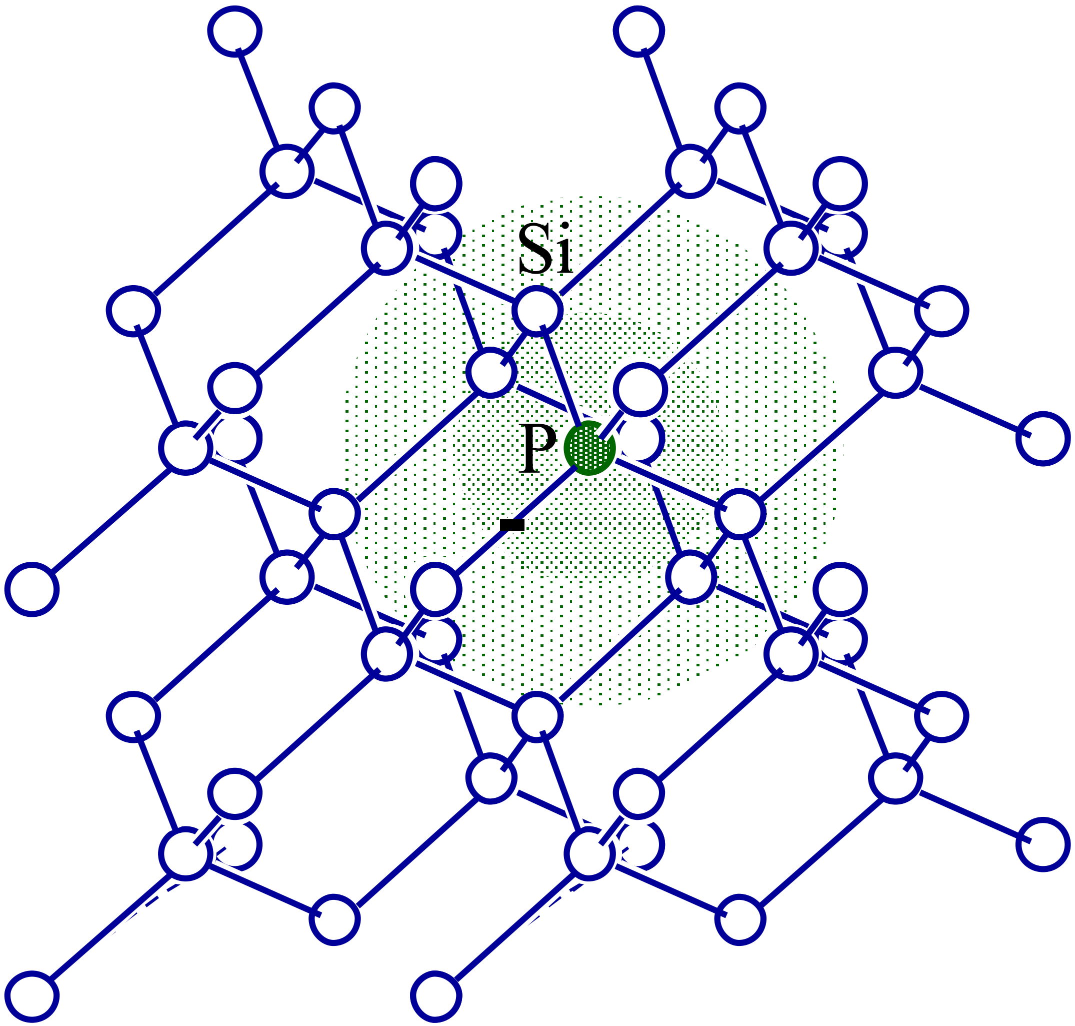
“Extrinsic” (Doped) Semiconductors

- Pure elemental semiconductors (Si, Ge, etc.) are used for devices where light or heat can be supplied to promote electrons.
- More useful devices are made using “doped” semiconductors — appropriate impurities are intentionally added to supply electrons (e.g., P) or holes (e.g., Al) which modify the band gaps and the conductivity can be controlled.

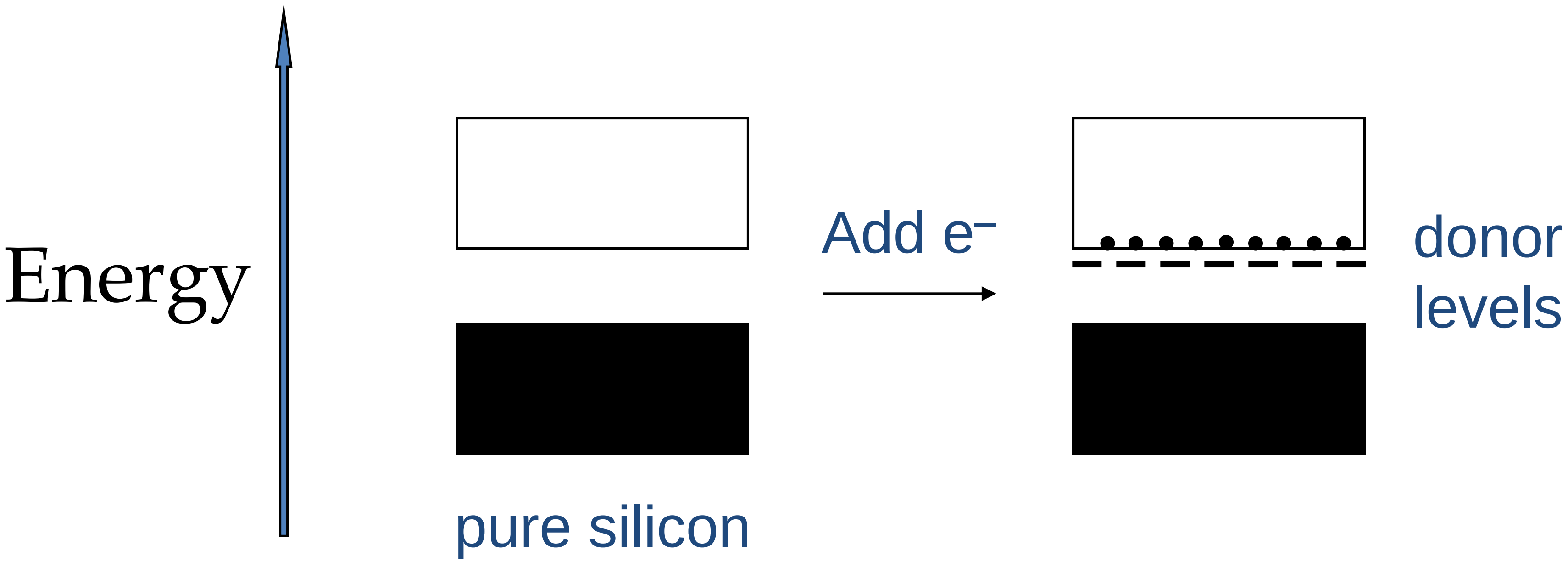
n-Type Semiconductors

- "Dope" with phosphorus. An electron is "left-over" after forming Si-P bonds.
- The added electrons are easily promoted from the "donor levels" at normal temperatures, so they can serve as charge carriers.
- Typical n-type devices contain on the order of 0.00001% P.

Phosphorus doped into Si: extra electron



n-Type Semiconductors

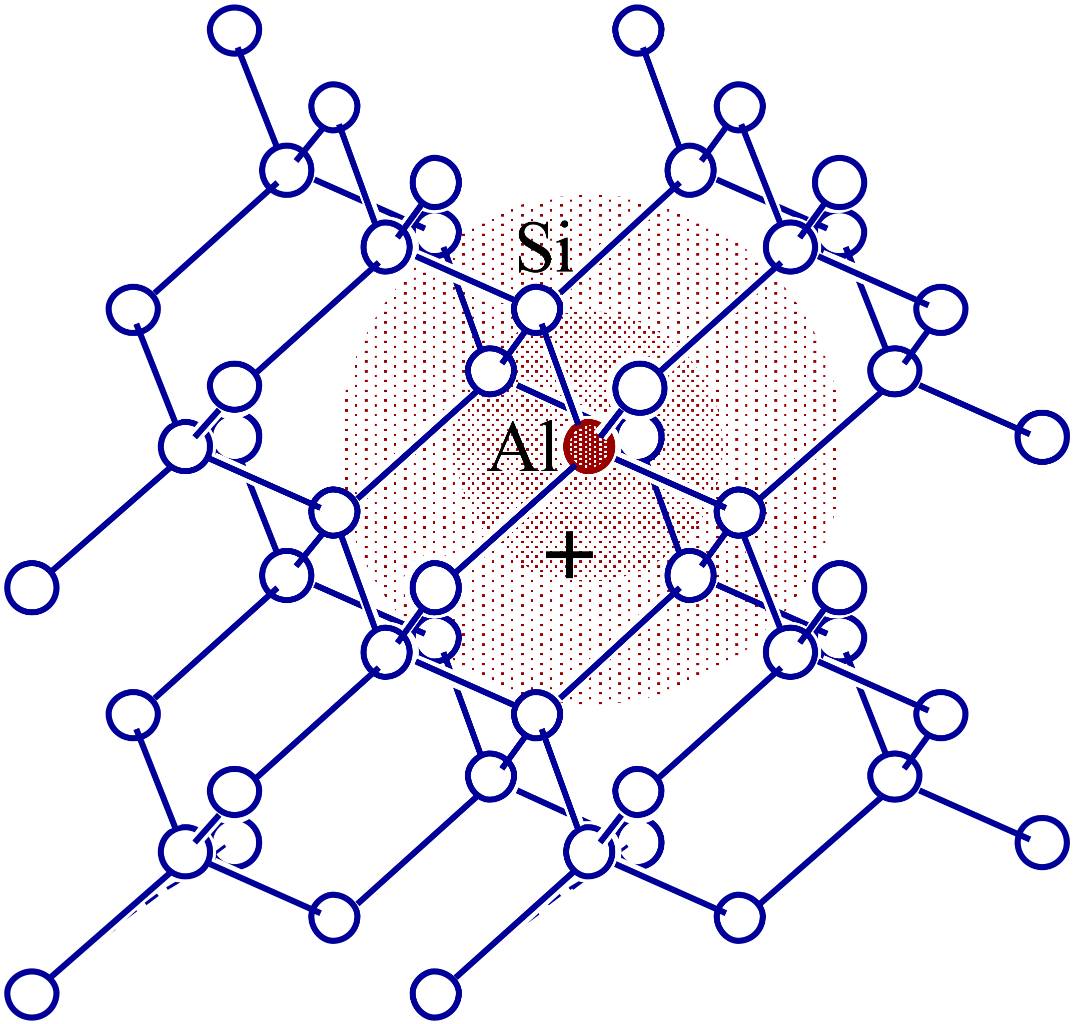


- Initially, valence band is full, conduction band is empty
- Added e^{-}'s must go in conduction band
- Extent of conductivity depends on # of electrons added.

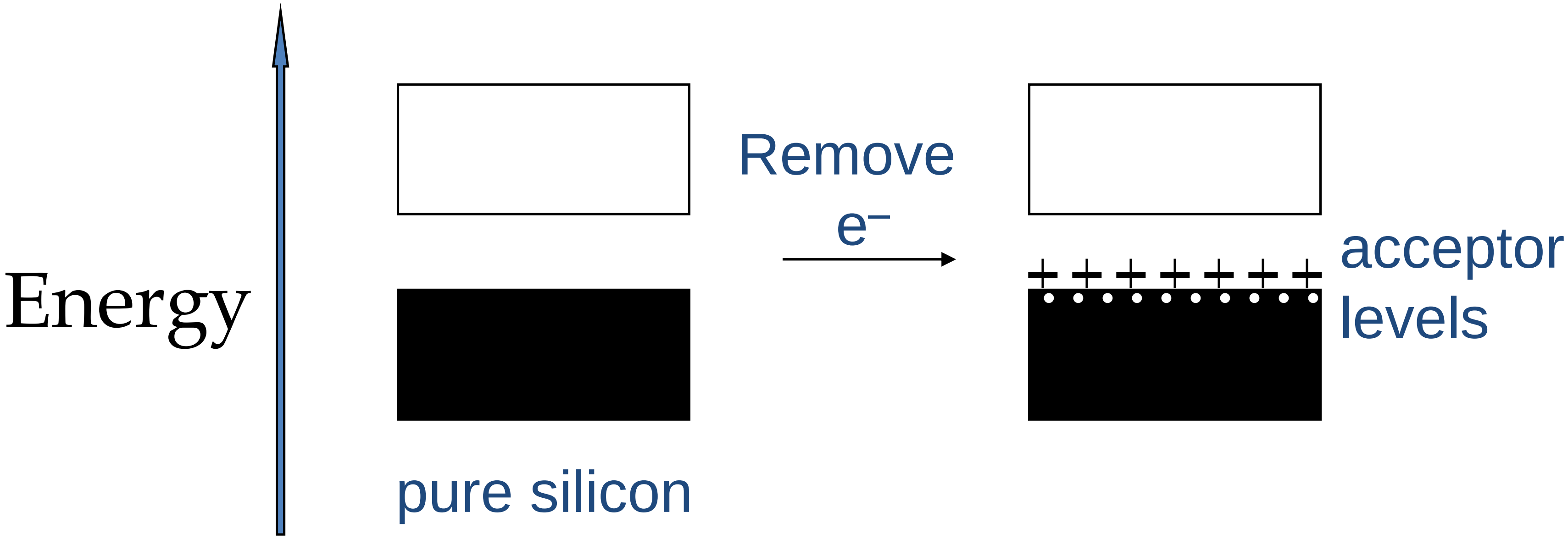
p-Type Semiconductors

- “Dope” with aluminum. Formation of Al-Si bonds “steals” an electron from Si.
- The holes allow “places for electrons to move into” within the valence band, so they serve as charge carriers
- Shallow “impurity” levels, as for n-type - electrons easily promoted at normal temperatures.
- Properties of n & p type differ slightly. Most devices contain combinations of both.

Aluminum doped into Si



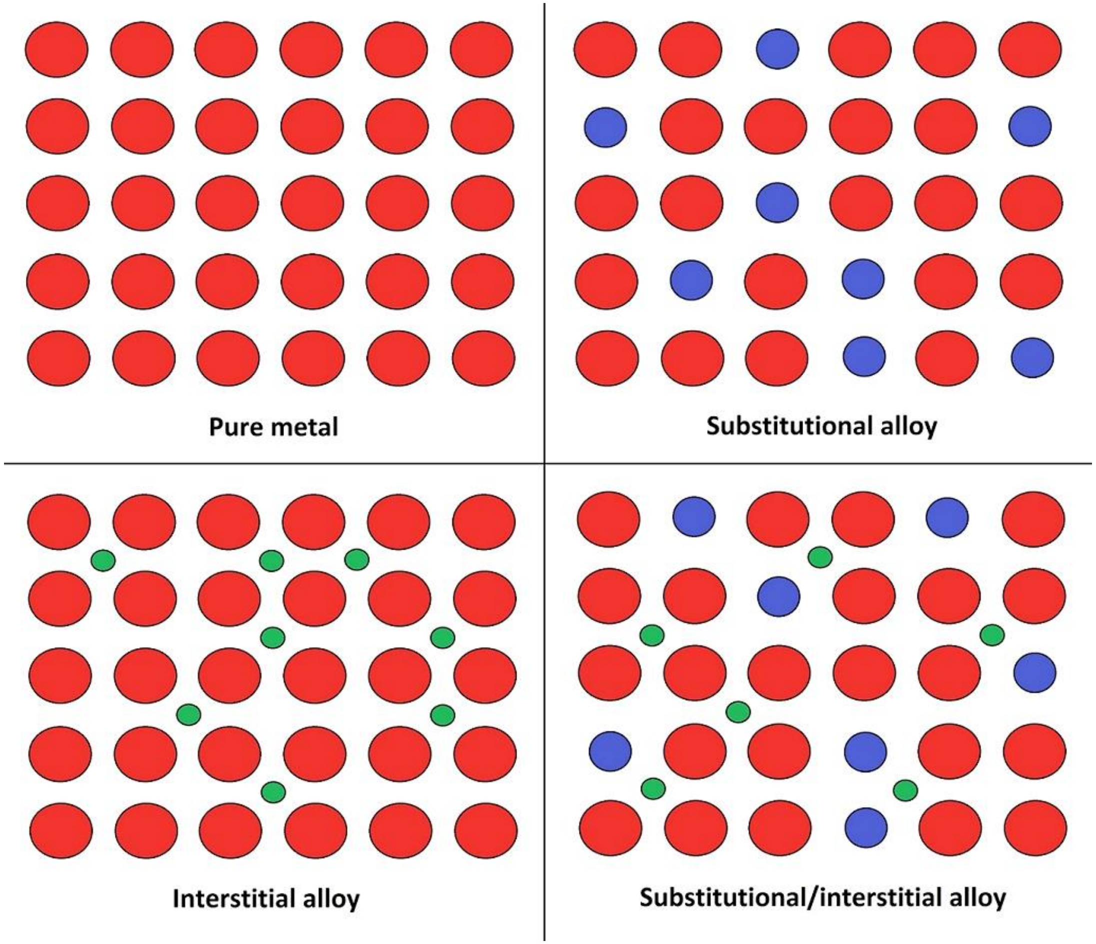
p-Type Semiconductors



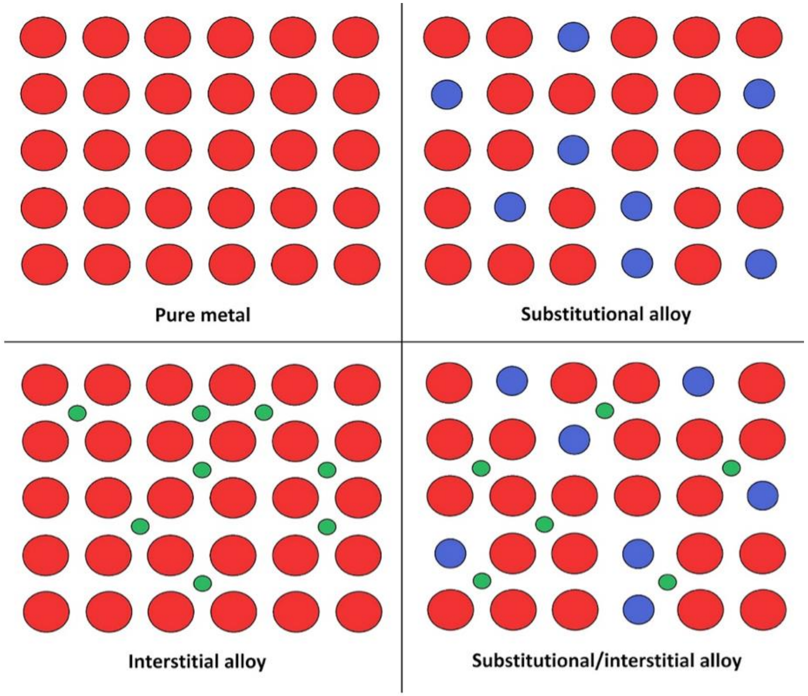
- Initially, valence band is full, conduction band is empty
- Removing e⁻'s leaves "holes" in valence band
- Number of electrons removed determines conductivity.

Alloys

Substitutional and Interstitial Alloys



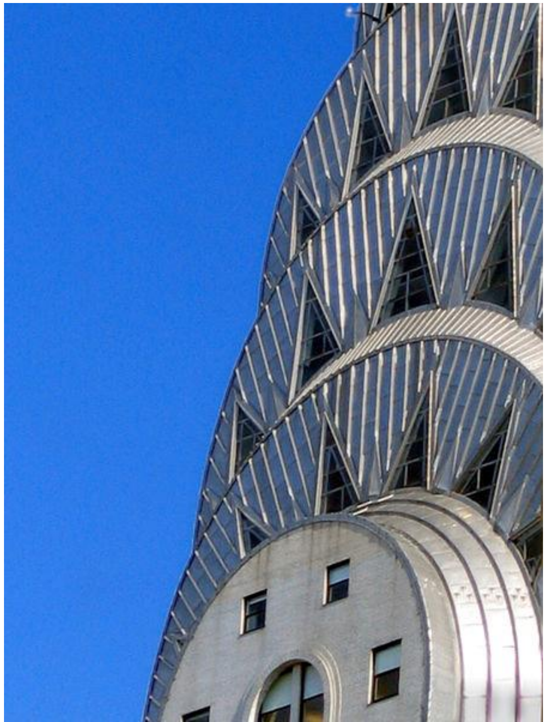
Types of Alloys



Substitutional and interstitial alloys

Examples of substitutional alloys include bronze and brass, in which some of the copper atoms are substituted with either tin or zinc atoms respectively. In the case of the interstitial mechanism, one atom is usually much smaller than the other and can not successfully substitute for the other type of atom in the crystals of the base metal. Instead, the smaller atoms become trapped in the spaces between the atoms of the crystal matrix, called the interstices. This is referred to as an interstitial alloy. Steel is an example of an interstitial alloy, because the very small carbon atoms fit into interstices of the iron matrix. Stainless steel is an example of a combination of interstitial and substitutional alloys, because the carbon atoms fit into the interstices, but some of the iron atoms are substituted by nickel and chromium atoms.[8]

Alloys—Stainless Steel



Alloys—Brass

Copper with some zinc

Bronze

Copper with some Tin

Composition of Alloys

- Bronze - probably the first intentionally created alloy - consists primarily of copper, usually with tin as the main additive: Musical instruments (cymbals), medals

  •Steel consists mostly of iron and has a carbon content between 0.2% and 2.1% by weight: Building, cutlery, surgical equipment

  •Brass consists of copper and zinc, the proportions of which can be varied to create a range of brasses with varying properties: Musical instruments, springs, screws, and rivets

  •Sterling silver (92.5% silver, the rest usually copper): Musical instruments (flute and saxophone), cutlery

  •10K (or 12K, or 14K, or anything under 24K) gold: Jewelry, police badges

  •Cupronickel nickels are made of nickel and copper, typically 75% copper, 25% nickel: Coinage, e.g. the US five-cent coin

  •Pewter (traditionally 85–99% tin, with the remainder consisting of copper, antimony, bismuth and lead): Tankards, spoons

  •Solder consists of lead and tin, the proportions of which can be varied to create a range of solders. The two most common alloys are 60/40 Sn/Pb and 63/37 Sn/Pb: Used to join together metal pieces in plumbing and electronic/electrical work

  •”Type” metal is an alloy of lead, tin and antimony in different proportions depending on the application. The proportions used are in the range: lead 50–86%, antimony 11–30% and tin 3–20%: Typesetting (part of the printing process) where the molten type metal is injected into a mold that has the shape of one or more letters or characters, these are then used to press ink onto paper

  •Wood's metal is composed of 50% bismuth, 26.7% lead, 13.3% tin, and 10% cadmium: Used by gunsmiths for making castings of firearm chambers