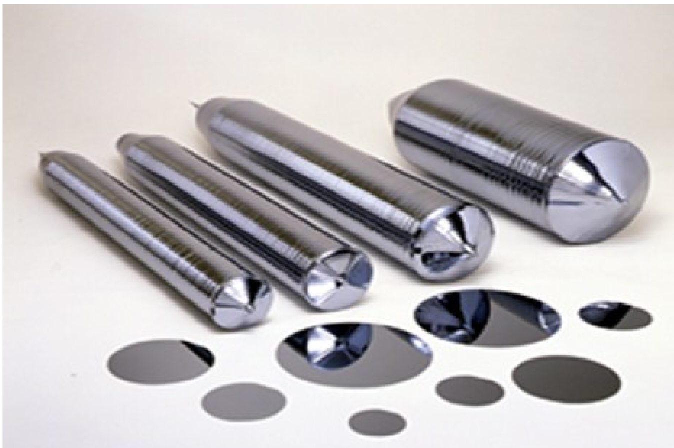
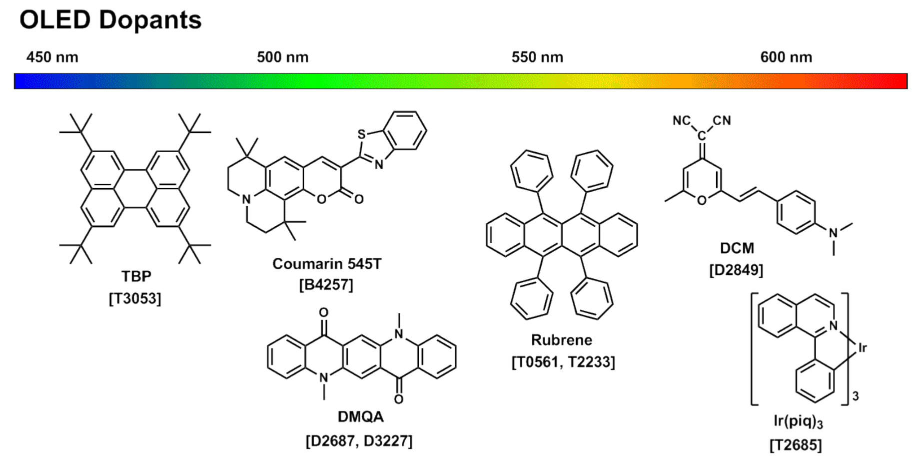
Solids

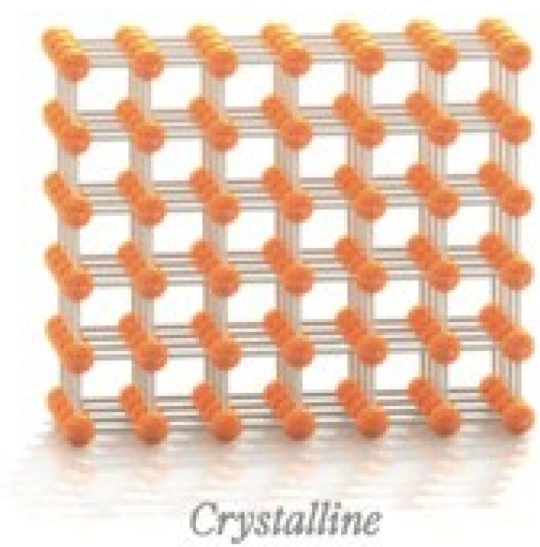



OLED Dopants
450 nm
500 nm
550 nm
600 nm
TBP
[T3053]
Coumarin 545T
[B4257]
DMQA
[D2687, D3227]
Rubrene
[T0561, T2233]
DCM
[D2849]
Ir(piq)3
[T2685]


intel

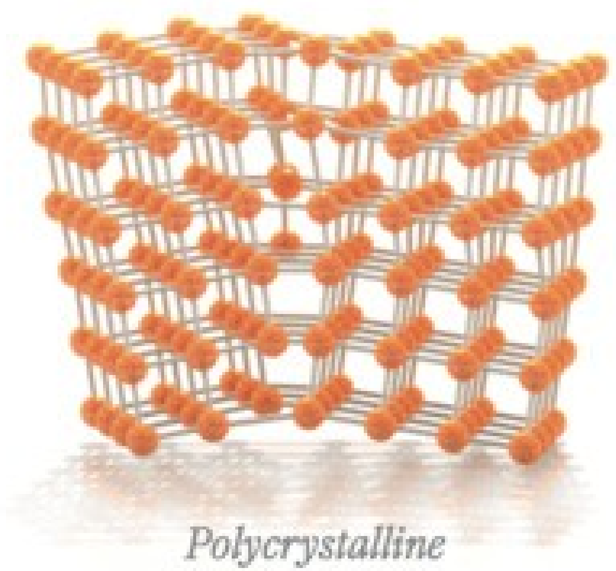
Types of solids

1. **Single crystal**



Periodicity throughout the material

2. **Polycrystalline**



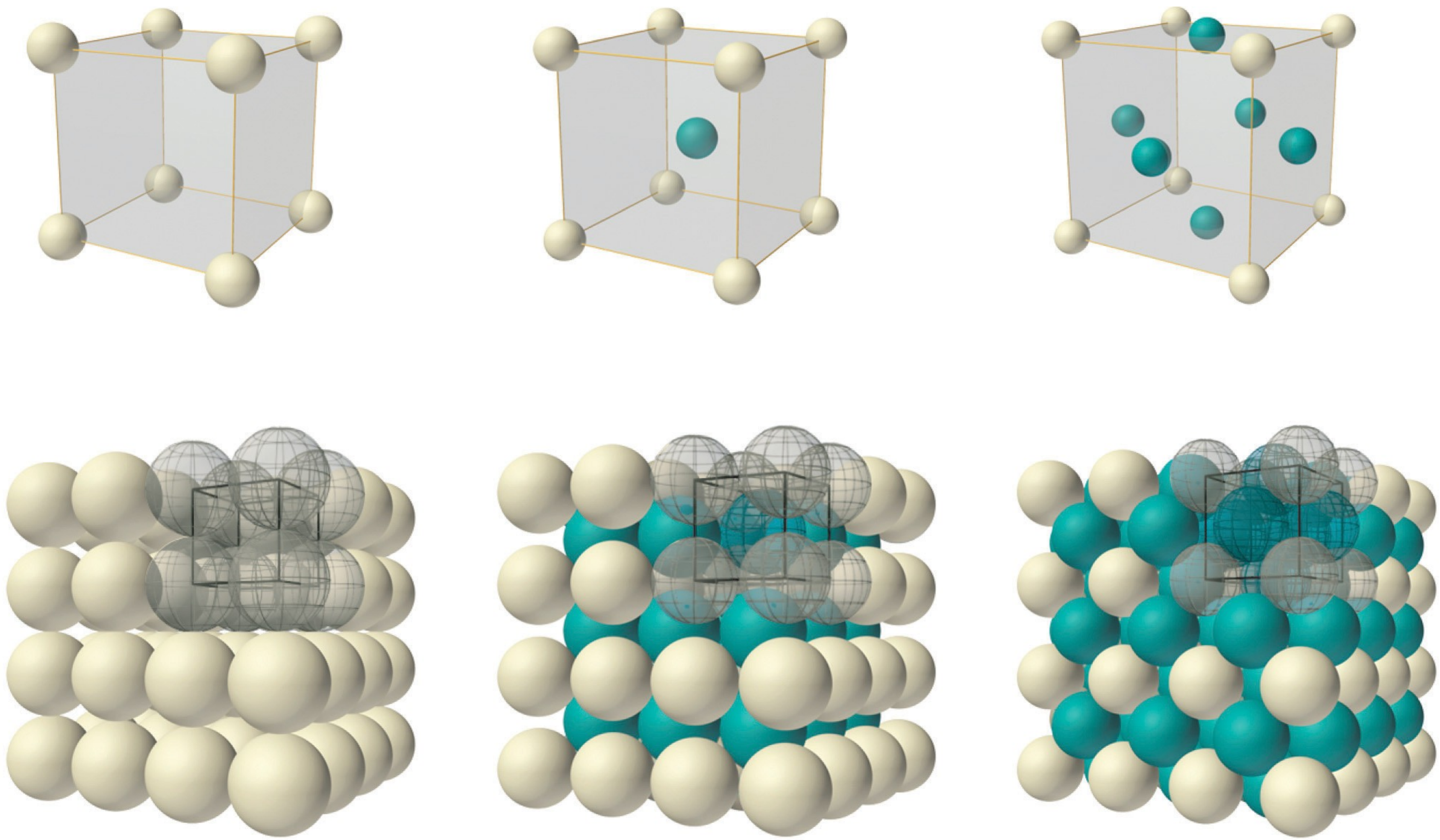
Multiple single crystal regions (grains)

3. **Amorphous**

No long range order

Crystal structures: lattices

O, F | Fe,Cr,Na | Au, Ni, Cu



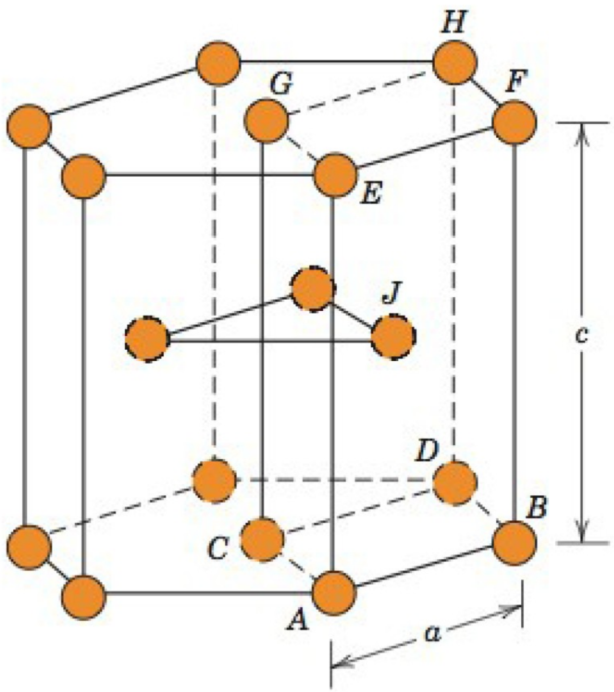
(a) Simple cubic **(b) Body-centered cubic** **(c) Face-centered cubic**

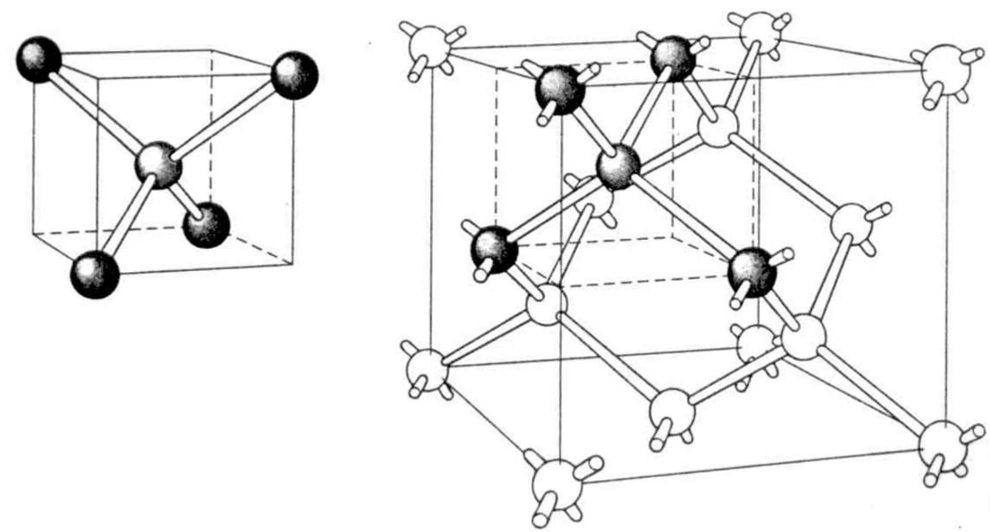
bcc **fcc**

Crystal structures: lattices

Co, Zn

diamond, Si, Ge



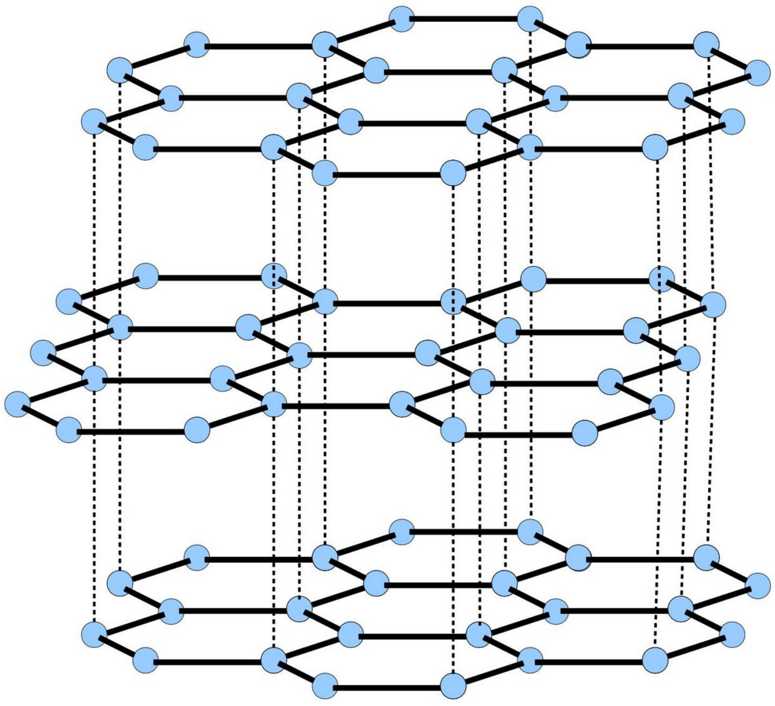


dc
diamond cubic

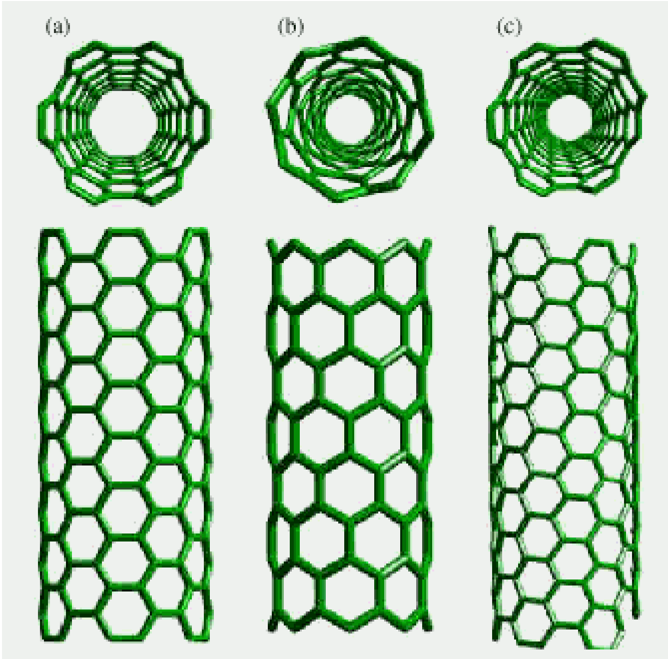
hcp
hexagonal closed packed

Crystal structures

Graphite



Nanotubes

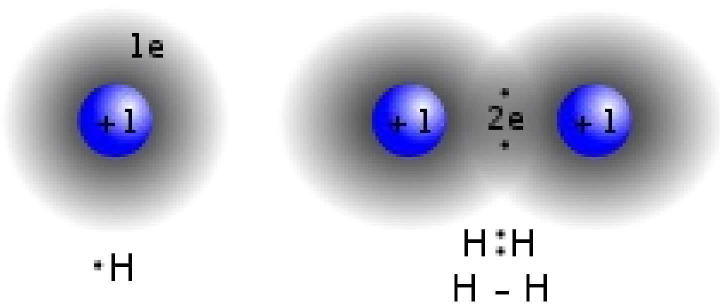


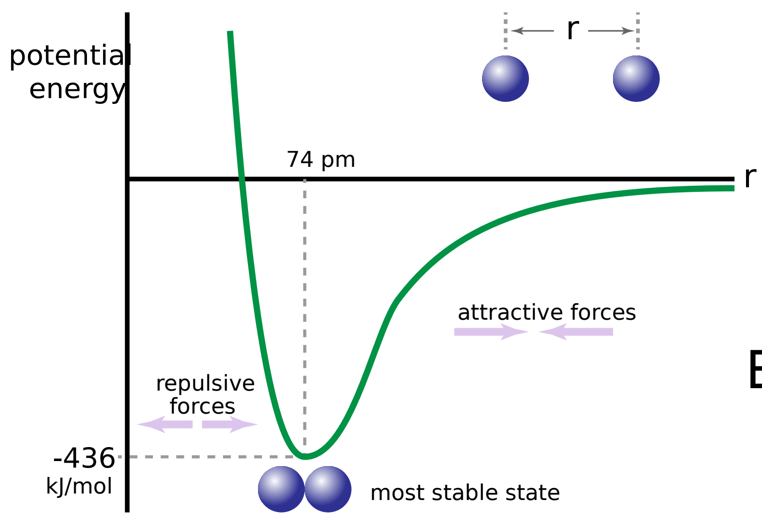
armchair **zig-zag** **chiral**

Covalent bonding

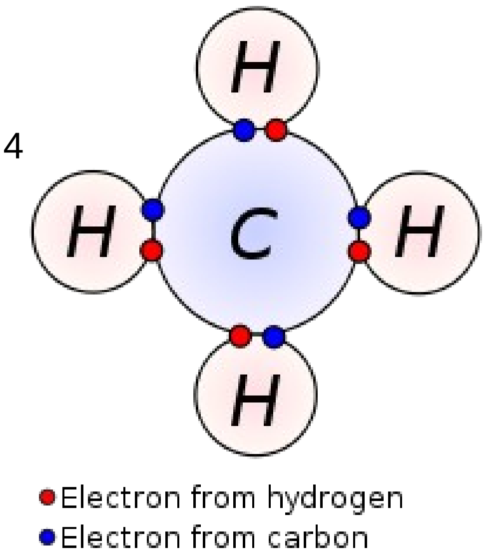
Electrons are <u>shared</u> between atoms

H_2





CH_4



$$E_i = E_{Coul} + E_{repuls} = \frac{-1}{4\pi\varepsilon_0}\frac{e^2}{r} + B\exp(-r/\rho)$$

Properties of covalent solids:

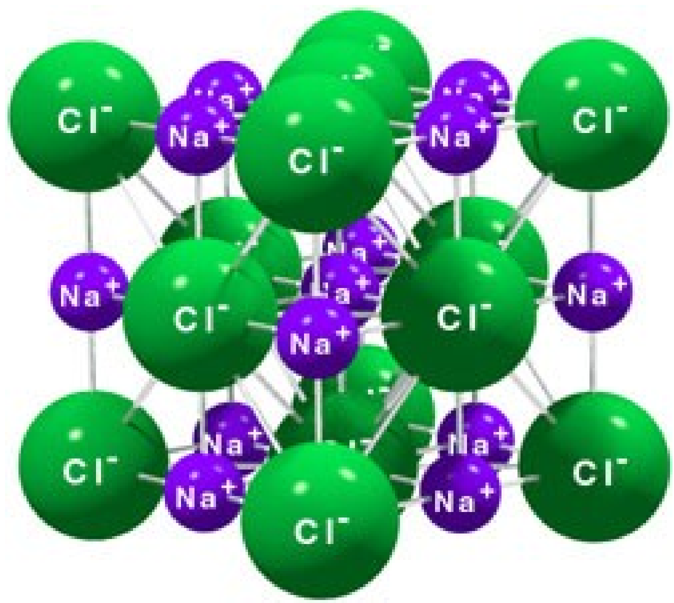
Bad thermal and electrical conductors (no free e^-)

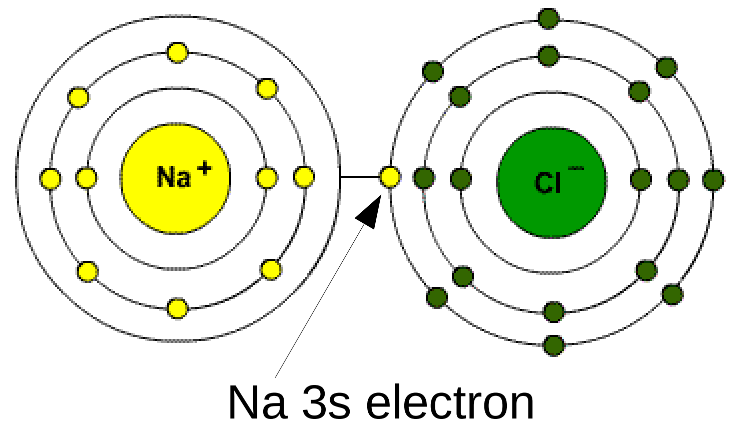
Hard and difficult to deform

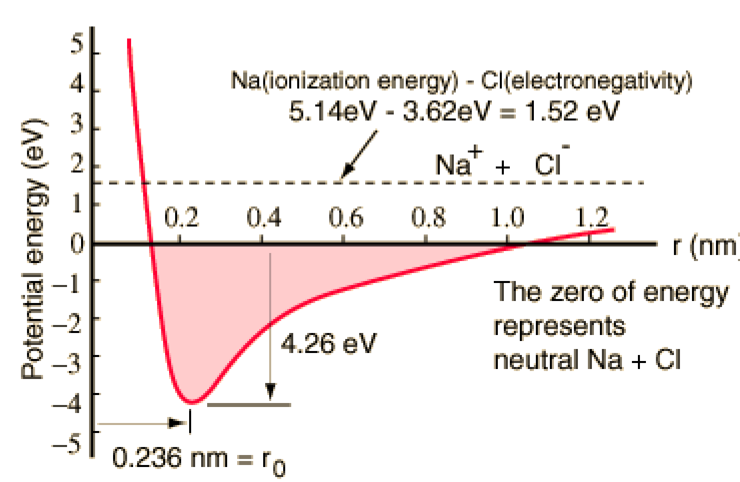
Ionic bonding

Electrons are <u>transferred</u> between atoms

$_{11}Na \rightarrow [Ne]\ 3s^1$ $\quad$ $_{17}Cl \rightarrow [Ne]\ 3s^2\ 3p^5$





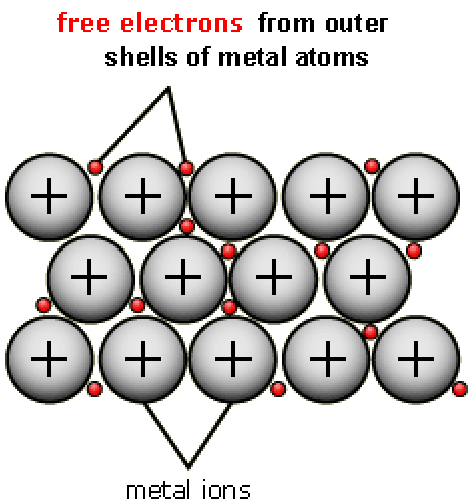


Properties of ionic solids:

- Bad thermal and electrical conductors (no free e-)
- Hard and fragile
- High melting and boiling point

Metallic bonding

Each valence electron is shared by many atoms. Strong attraction forces between the positive ions and the delocalised electrons. The number of free electrons varies from metal to metal ~ one per atom



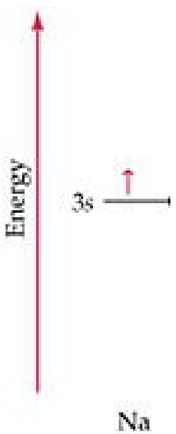
Properties of metals:

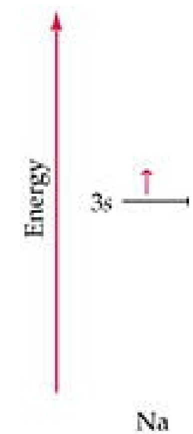
Good thermal and electrical conductors (they have free e-)
n~ 10^{22} carriers/cm^3

Ductile

Band formation

What happens to the energy levels of atoms when they bond?

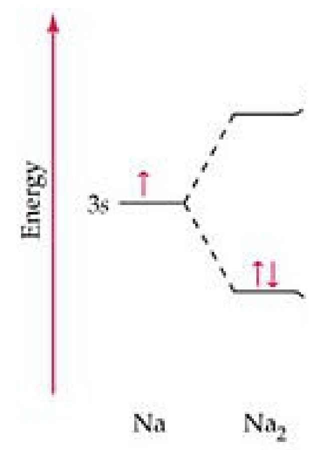




When the atoms are far apart, the energy of a particular level is the same for each atom.

Band formation

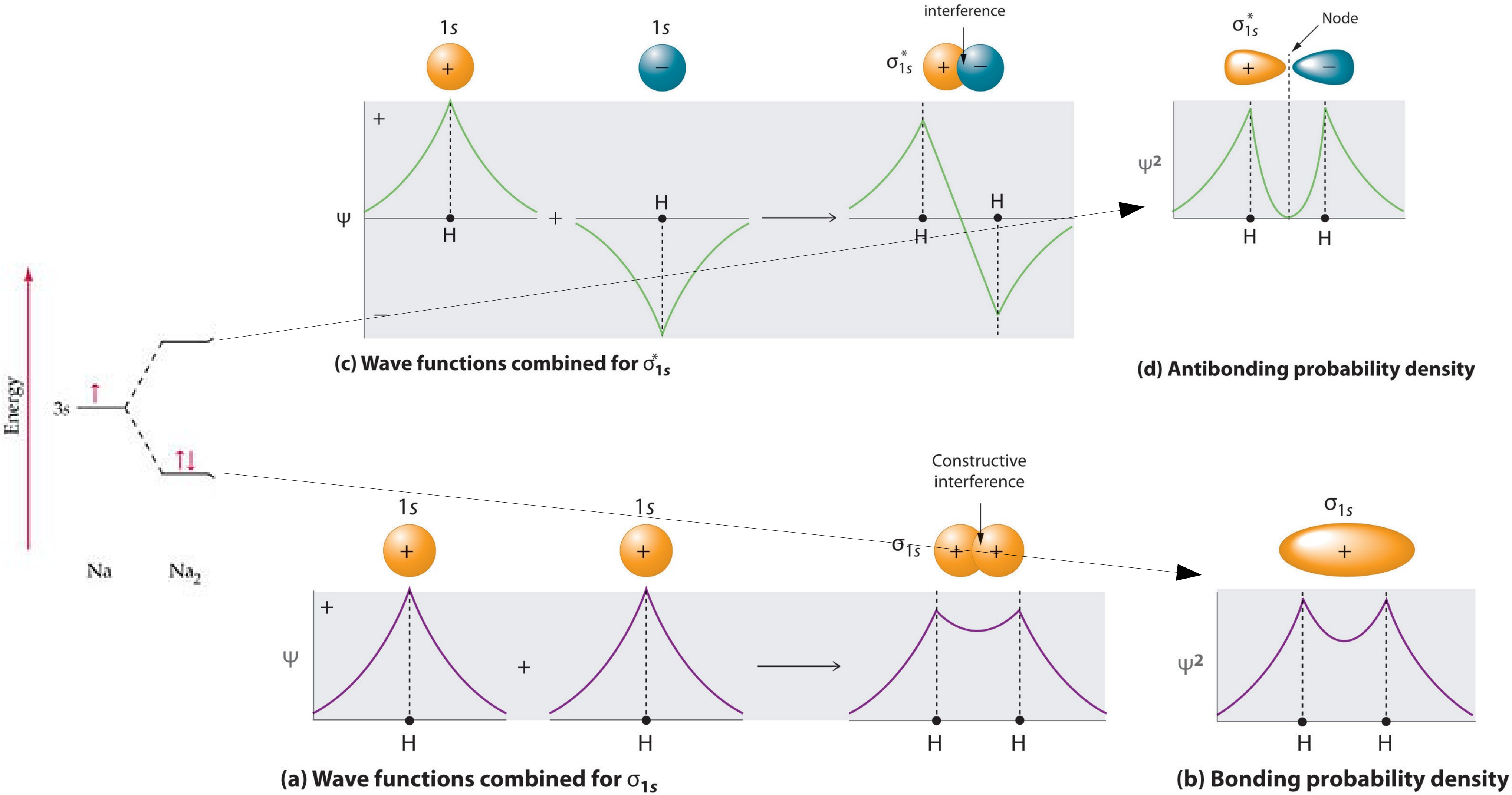
What happens to the energy levels of atoms when they bond?



When two atoms are brought closer together, the energy level for each atom changes because of the influence of the other atom.

→ the level splits into two levels of slightly different energies for the two-atom system.

Energy level splitting

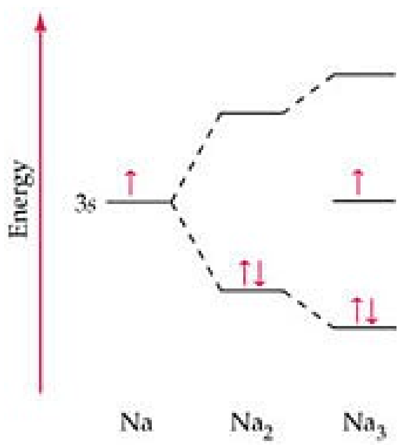


For symmetric wavefunction → The bonding state piles up electronic charge in the middle of the bond and lowers the total energy of the system.

For antisymmetric wavefunction →The antibonding state piles up electronic charge around the nuclear sites, increasing the total energy of the system.

Band formation

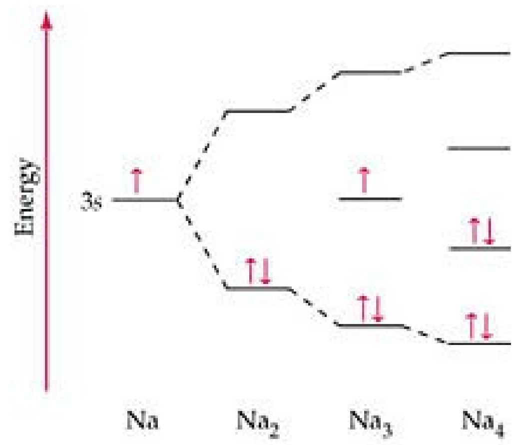
What happens to the energy levels of atoms when they bond?



If we bring three atoms close together, a particular energy level splits into three separate levels of slightly different energies

Band formation

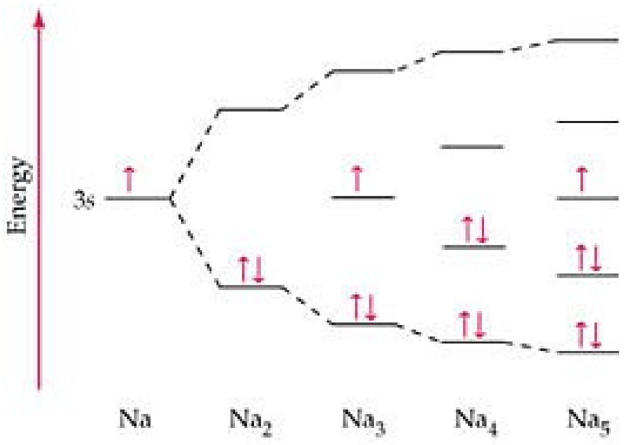
What happens to the energy levels of atoms when they bond?



If we bring four atoms close together, a particular energy level splits into four separate levels of slightly different energies

Band formation

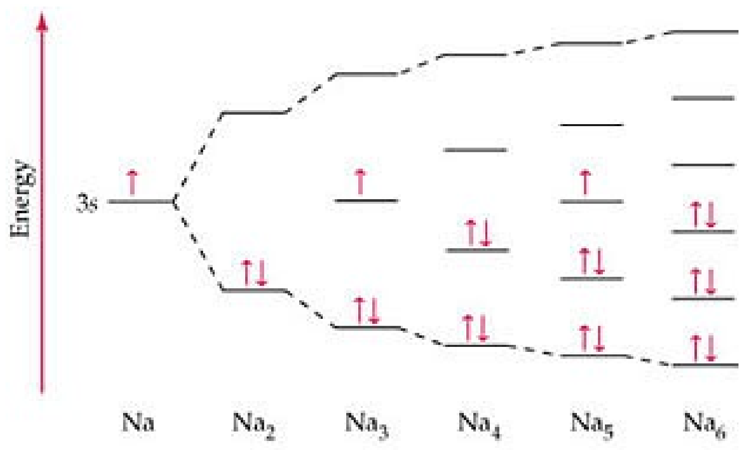
What happens to the energy levels of atoms when they bond?



And so on..

Band formation

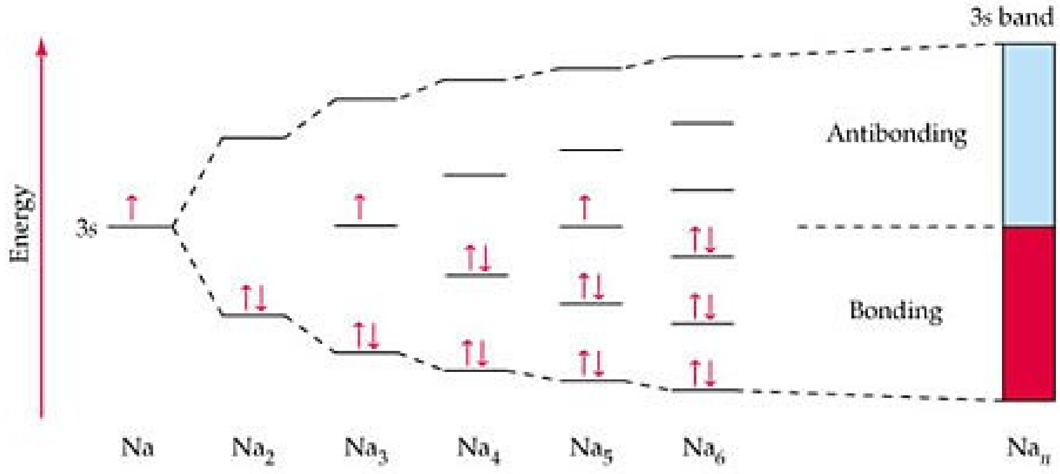
What happens to the energy levels of atoms when they bond?



And so on..

Band formation

What happens to the energy levels of atoms when they bond?



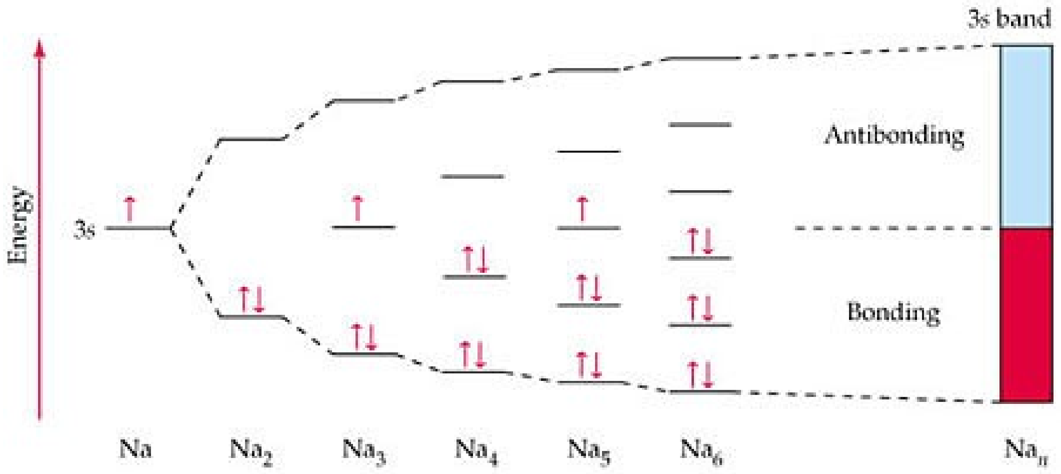
N identical atoms → a particular energy level in the isolated atom splits into N different, closely spaced energy levels.

In a macroscopic solid, N~10^{23} → each energy level splits into a very large number of levels called a **band**.

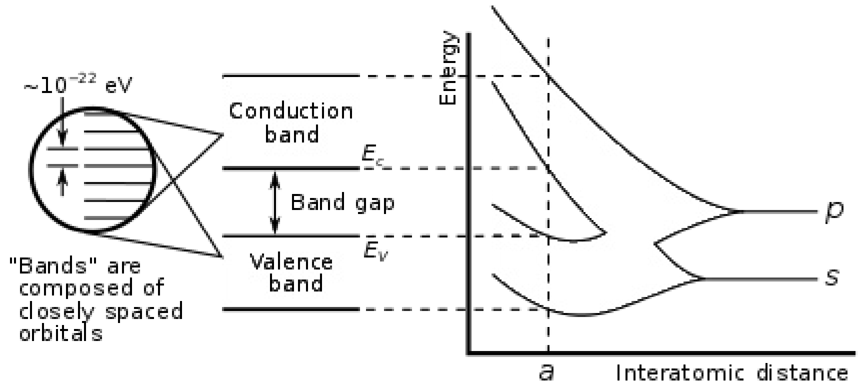
Band formation

What happens to the energy levels of atoms when they bond?

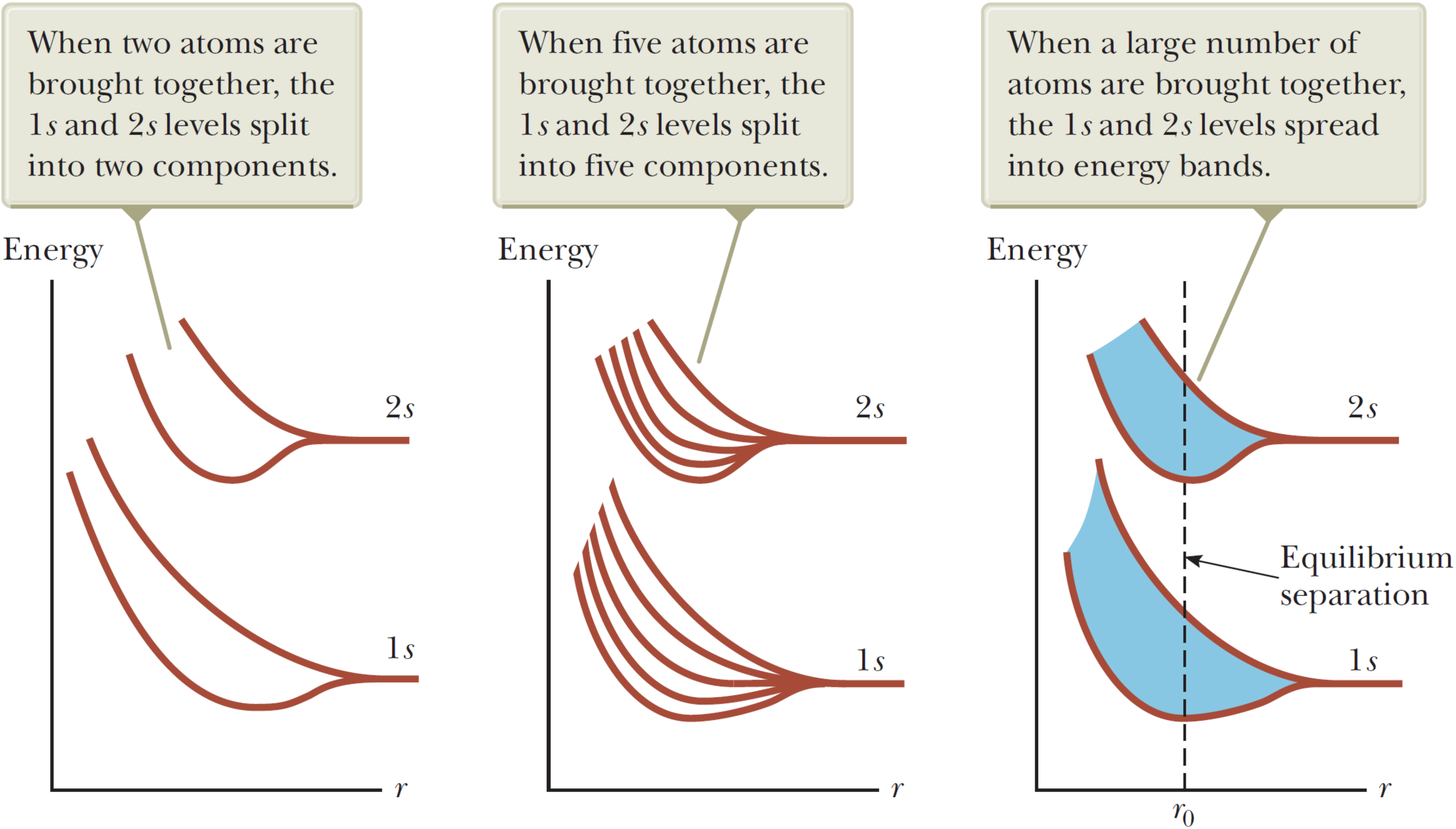
Na



Si



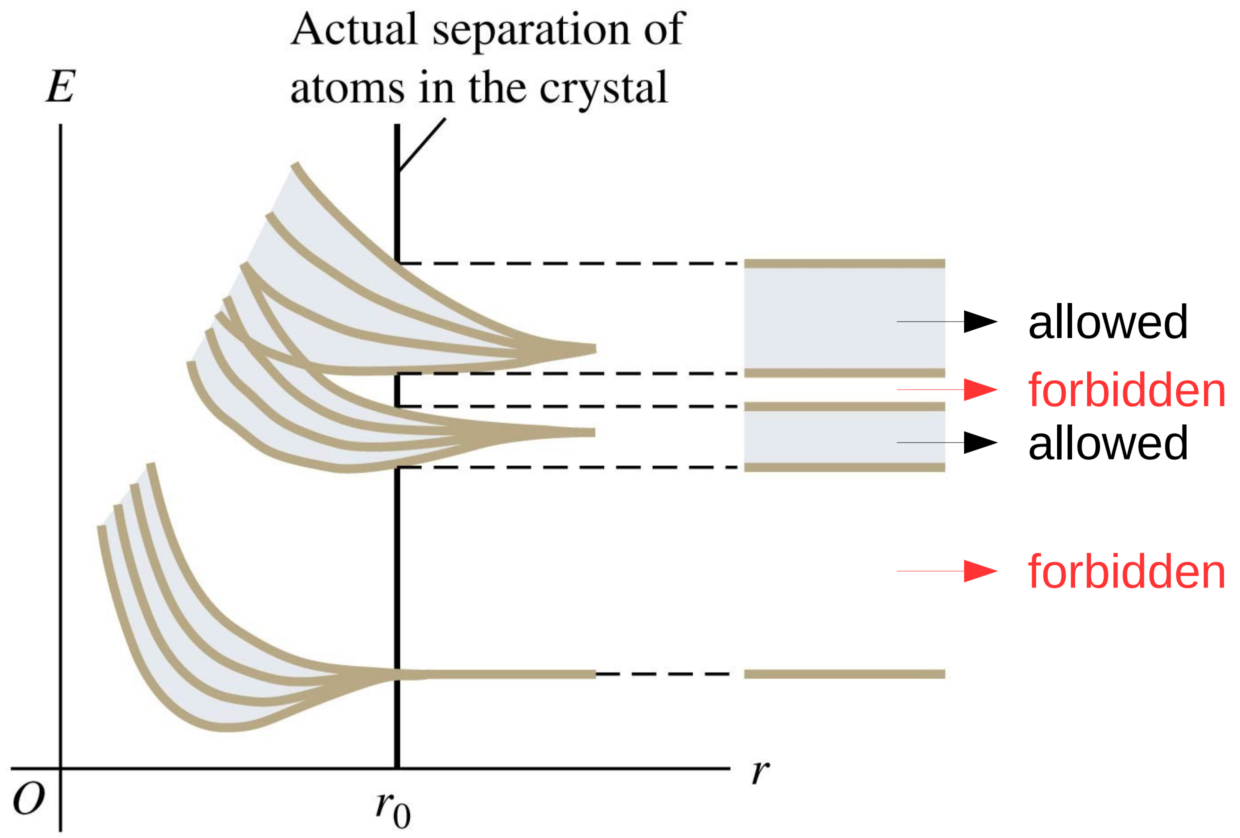
→ They form energy ***bands***, consisting of many states close together but slightly split in energy.



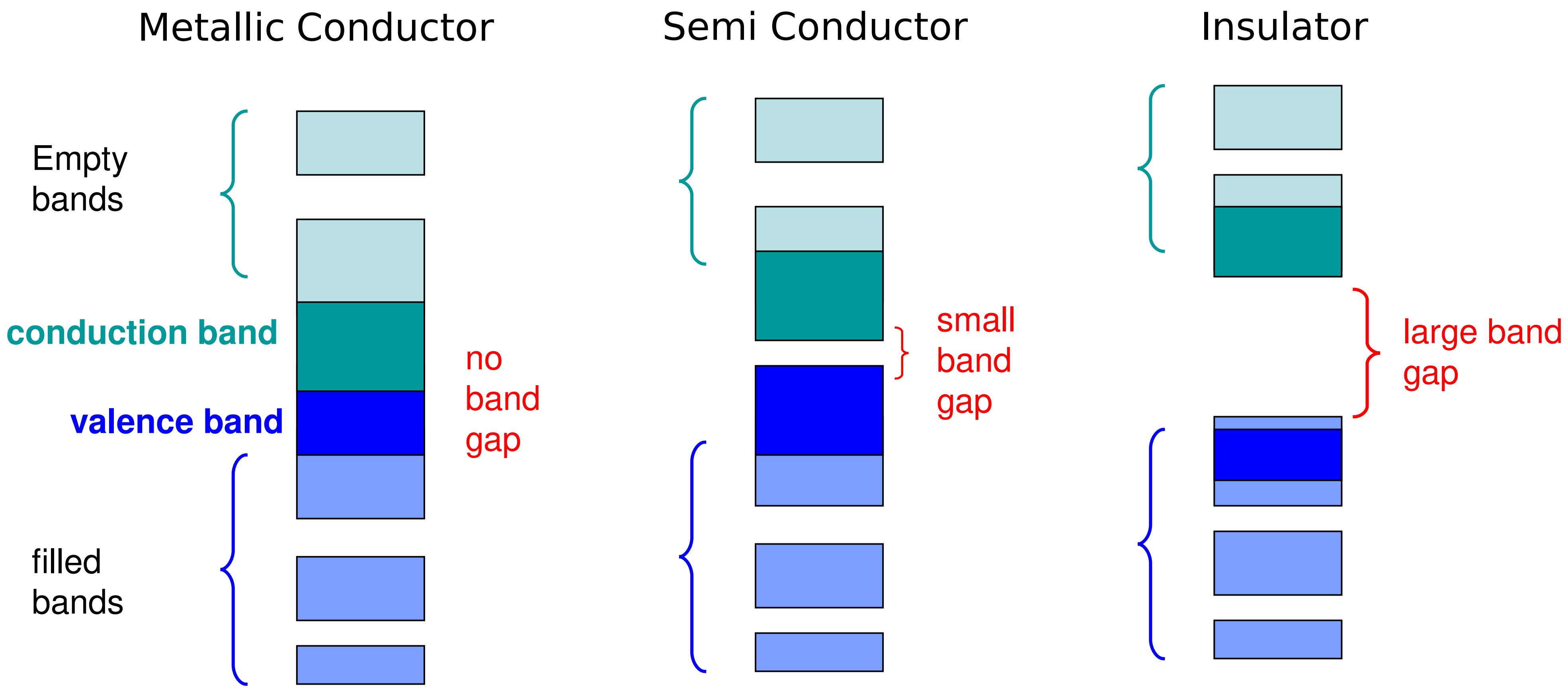
When two atoms are brought together, the 1s and 2s levels split into two components.
When five atoms are brought together, the 1s and 2s levels split into five components.
When a large number of atoms are brought together, the 1s and 2s levels spread into energy bands.
Energy
2s
1s
r
Energy
2s
1s
r
Energy
2s
1s
Equilibrium separation
r
r0

Energy bands

- As the distance *r* between atoms in a crystal decreases, the energy levels spread into **bands**.
- In practice, bands form a *continuous* distribution of energies within a band.
- Between adjacent energy bands are gaps where there are no allowed energy levels.



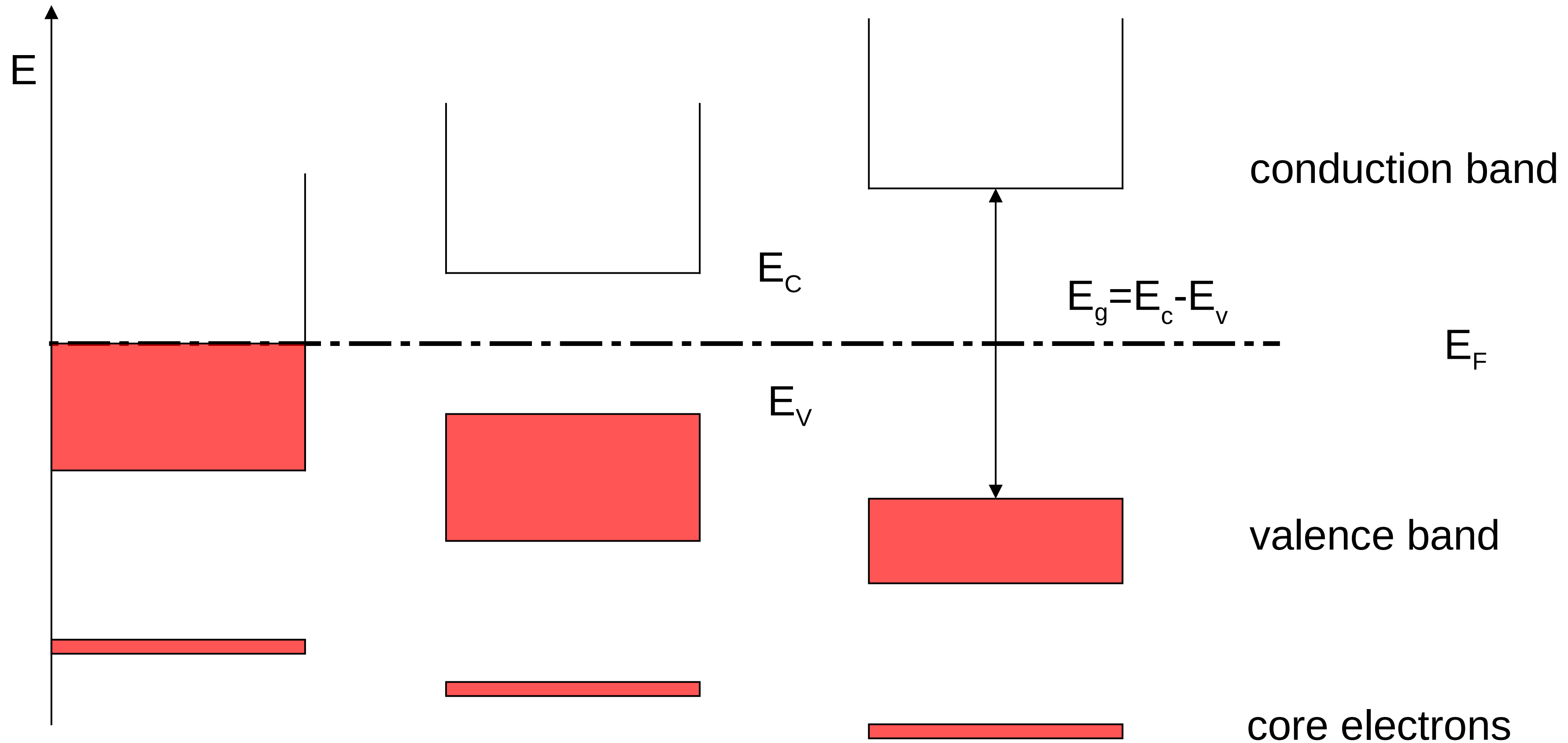
Band diagrams



VALENCE BAND: Last band containing electrons
CONDUCTION BAND: First band having unoccupied states

Conduction properties

Only partly filled electronic band can contribute to electric current



Metal, **E_g=0**

Semiconductor, **E_g<5 eV**

Insulator, **E_g>5 eV**

Cu, Fe

Si: **E_g=1.12 eV**

Ge: **E_g=0.66 eV**

SiO_2

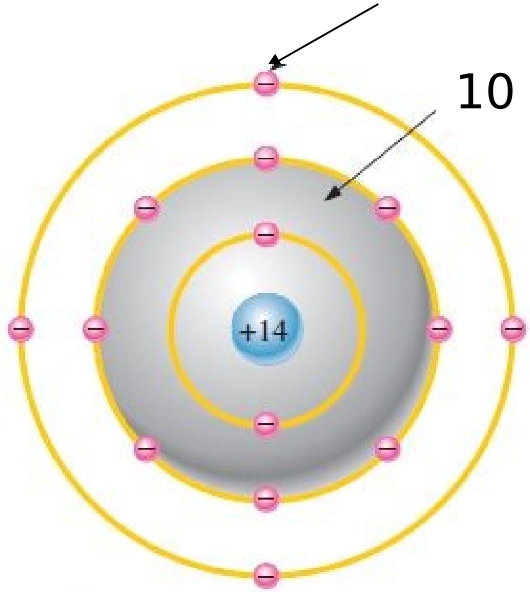
E_c→ the bottom of the conduction band

E_v→ the top of the valence band

Silicon atom

4 valence electrons: $3s^2p^2$

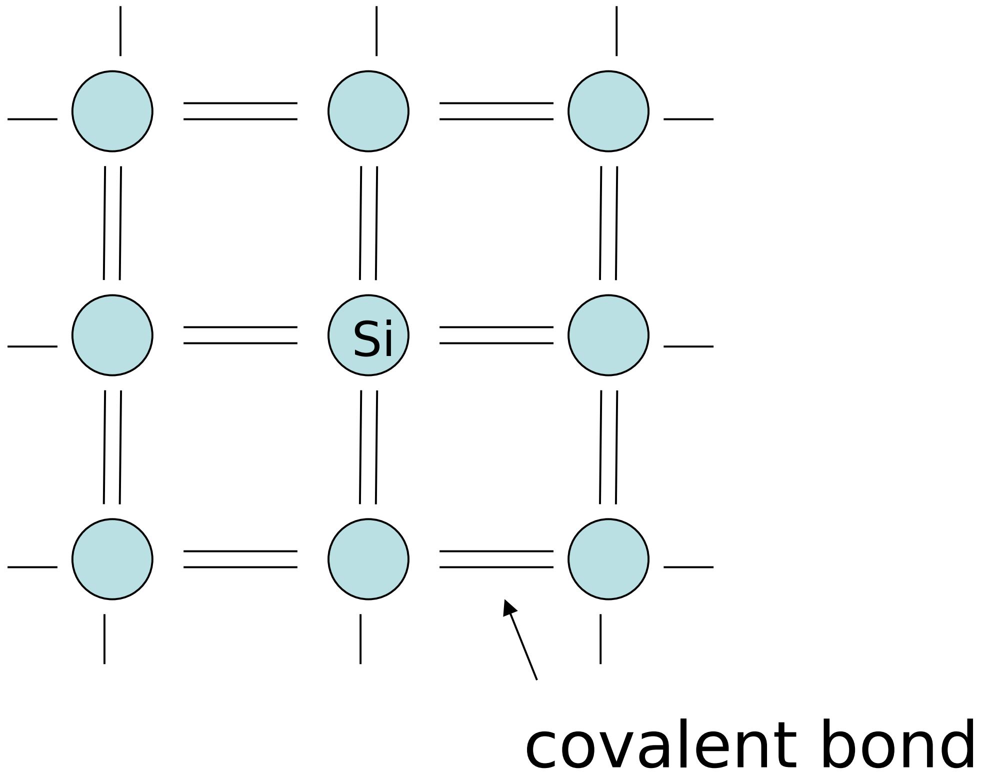
10 core electrons: $1s^22s^2p^6$



The 4 valence electrons are responsible for forming covalent bonds

“2D” model of Si crystal

At T=0 K all valence e are bonded → no free e → INSULATOR

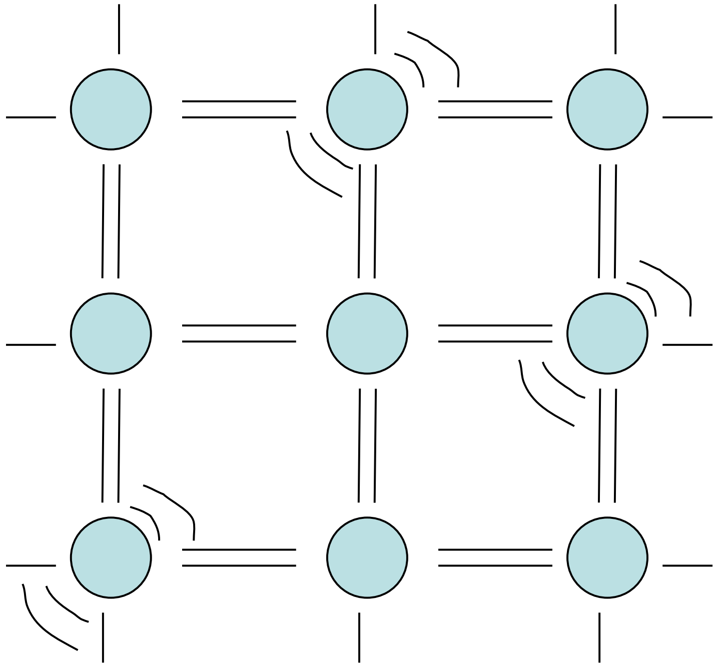


“2D” model of Si crystal

At T> 0 K Si atoms vibrate in the lattice

→ some covalent bonds break

→ free valence e

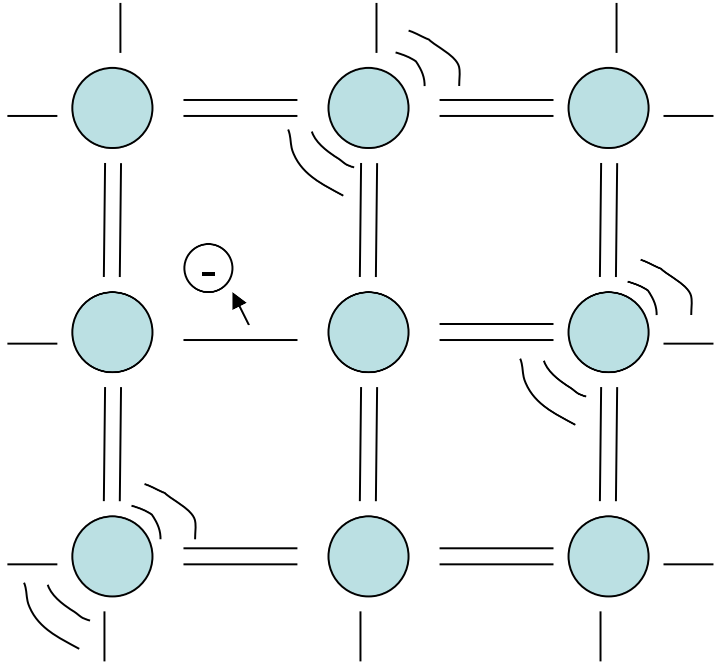


Si as intrinsic semiconductor

At T> 0 K Si atoms vibrate in the lattice

→ some covalent bonds break

→ free valence e



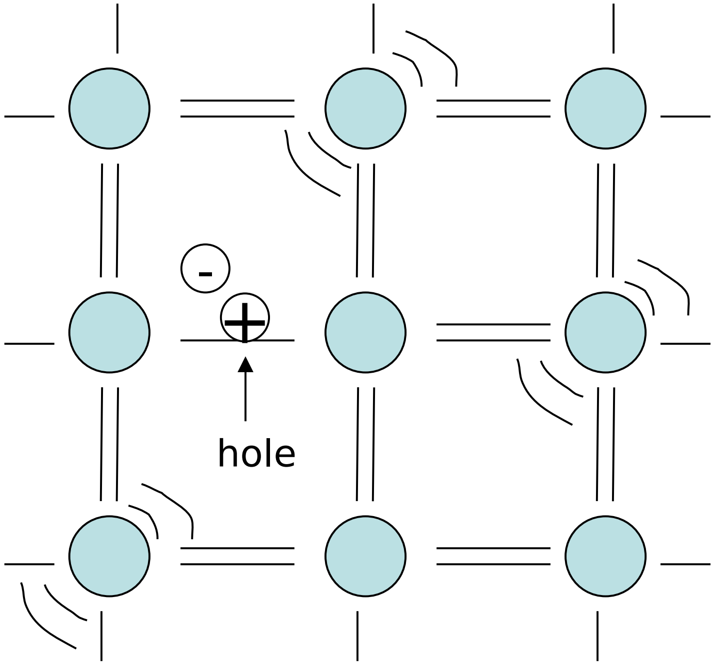
- = free electron

Si as intrinsic semiconductor

At T> 0 K Si atoms vibrate in the lattice

→ some covalent bonds break

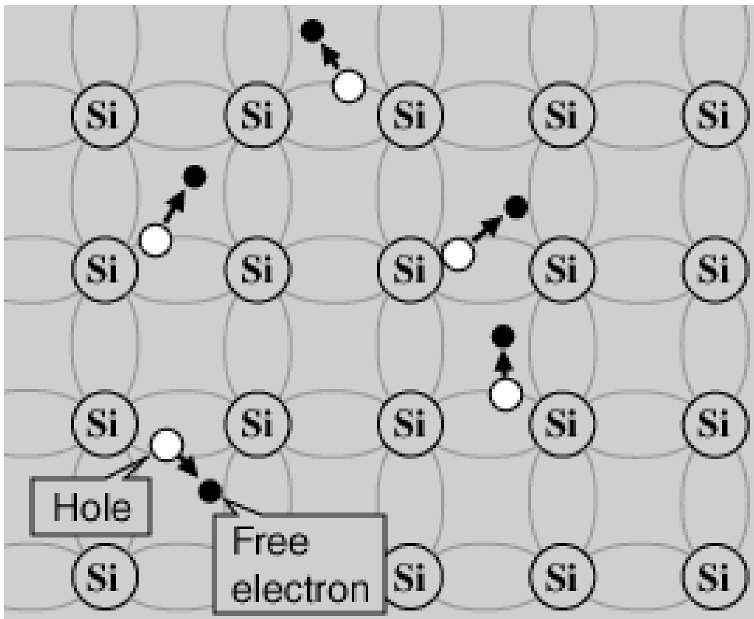
→ free valence e → missing e → hole

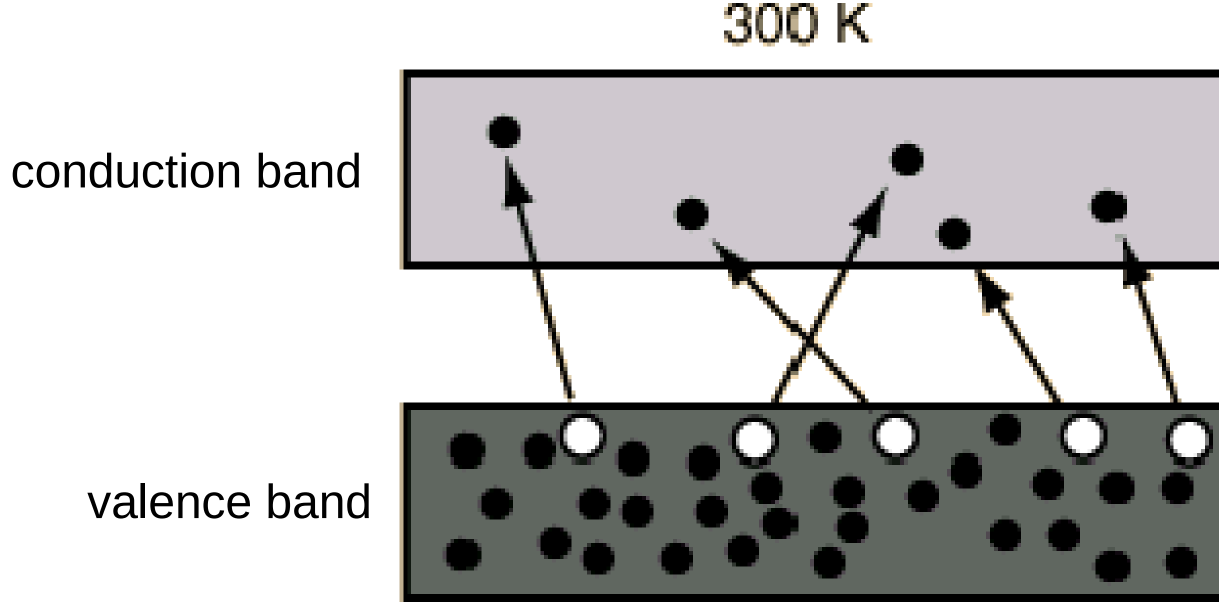


The hole is a missing negative charge and has a charge of **+1**.

⊕ = a hole

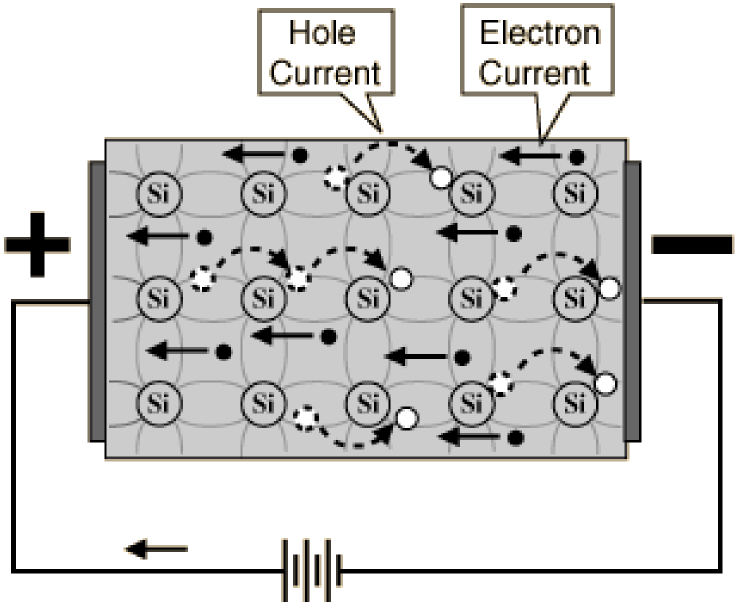
Si as intrinsic semiconductor

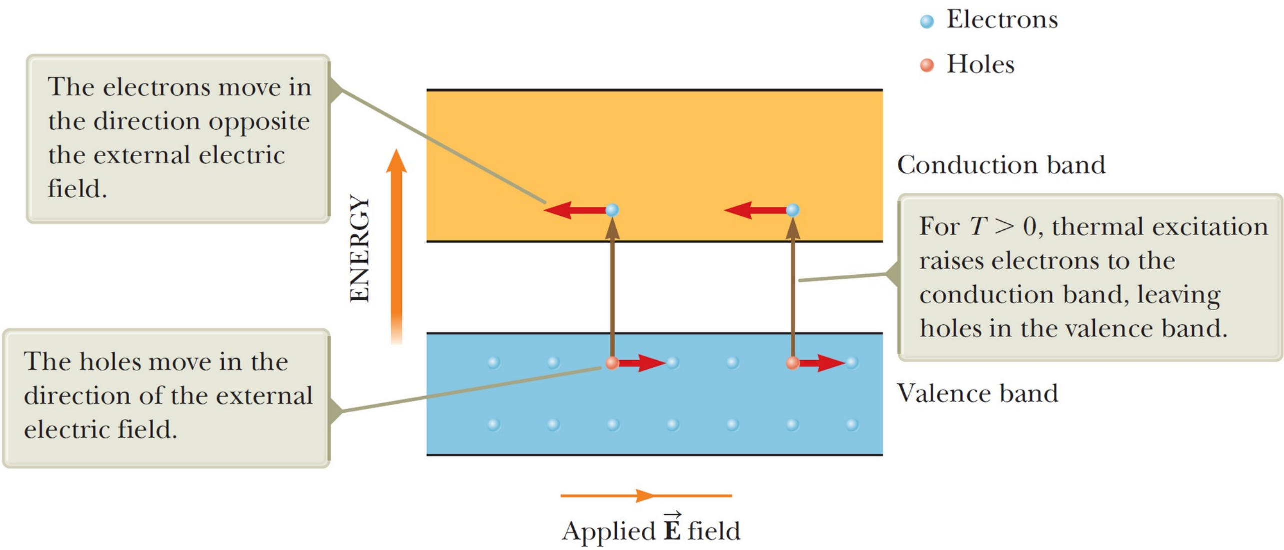




- Electrons are thermally excited into the conduction band
- Electron – hole pairs are created.
- Two types of carriers: electrons and holes both contribute to conduction

Current flow in Si





Conductivity is proportional to the number of free electrons and the number of holes.

Charge carrier density

electrons (negative)
holes (positive)

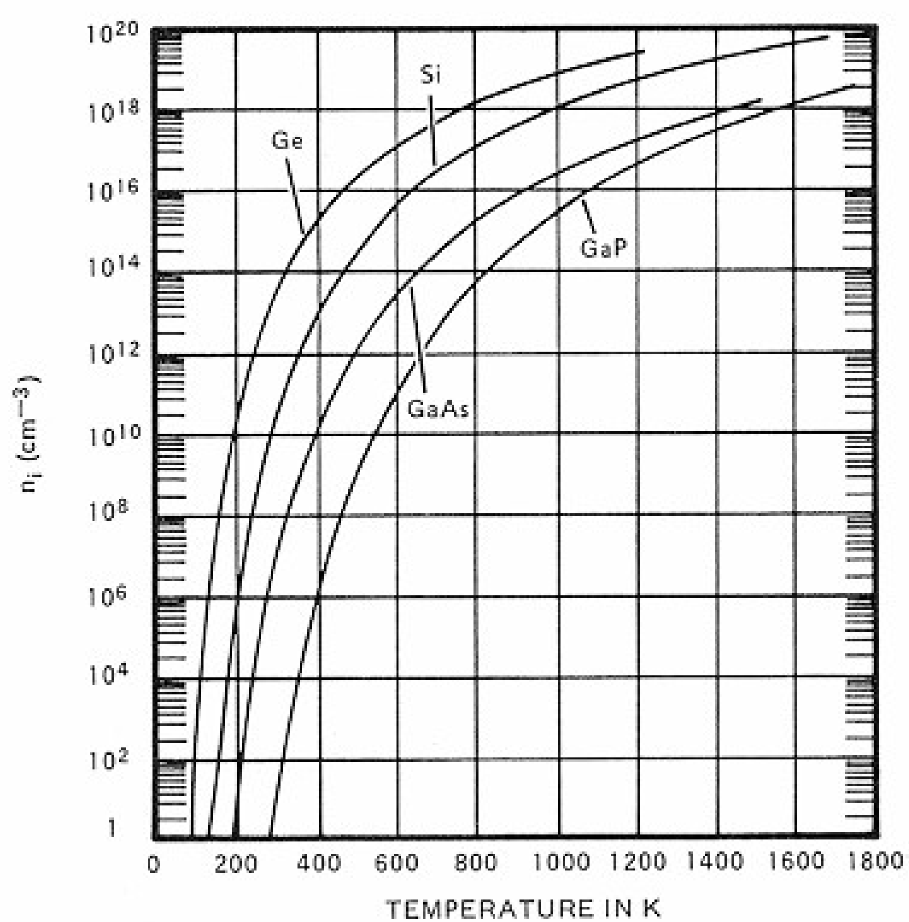
$$n = p = n_i = \sqrt{N_C N_V}\, e^{-\frac{E_g}{2 k_B T}}$$

The density of carriers increases with T, and so does the conductivity.

- N_C and N_v depend on the semiconductor and the temperature (density of states)

Example: Si at 300 K
$N_C = 2.8 \times 10^{19}$ cm^{-3}
$N_V = 1.04 \times 10^{19}$ cm^{-3}

- Boltzmann constant
$k_B = 1.38 \times 10^{-23}$ J/K $= 8.614 \times 10^{-5}$ eV/K



Intrinsic semiconductors

A problem: Very few free electrons/holes at room temperature

$n=p=6.6x10^9$ per cm^3, but $n_{Si} = 5x10^{22}$ per cm^3 *(see exercise 14 (a)).*

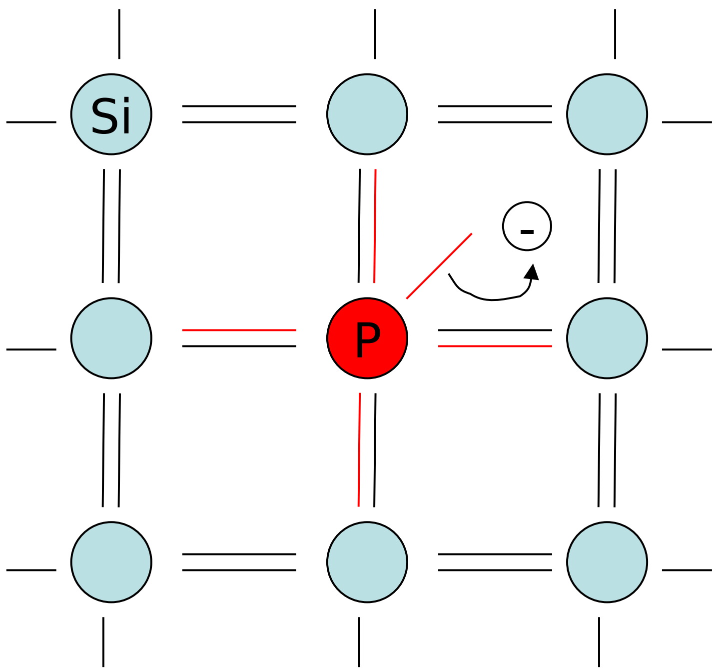
$n/n_{Si} = 3x10^{-13}$ (*number of free electrons per Si atom at RT*) → very few Si bonds are broken!

- **How to increase the conductivity?**

By doping → extrinsic semiconductor

Extrinsic semiconductors: n-type

add atoms from *column V* of the periodic table



Column V elements have 5 valence electrons

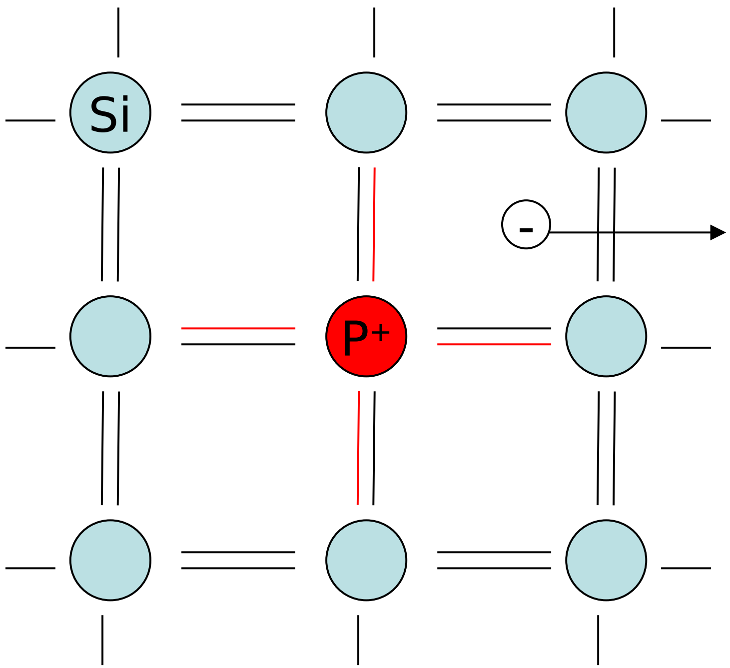
Four of the electrons form covalent bonds with Si, but the 5^{th} electron is unpaired.

Because the 5^{th} electron is weakly bound, it almost always breaks away from the P atom.

This is now a free electron.

Extrinsic semiconductors: n-type

add atoms from *column V* of the periodic table



The phosphorus atom has *donated* an electron to the semiconductor (Column V atoms are called *donors*)

The phosphorus is *missing* one of its electrons, so it has a positive charge (+1)

The phosphorus ion is bound to the silicon, so this +1 charge can't move!

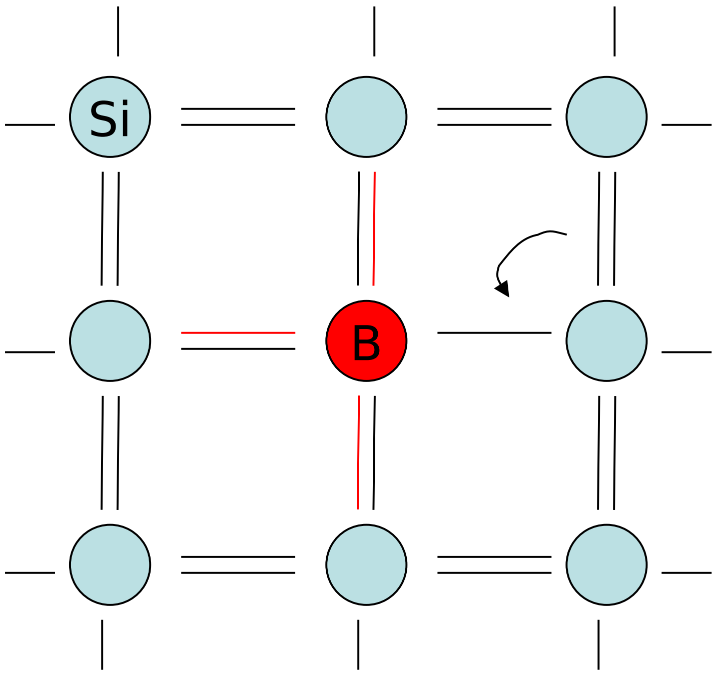
The number of "extra" electrons is equal to the number of phos. atoms:
$n = N_d$

n-type semiconductor (donor):

more electrons than holes ($n>p$)

Extrinsic semiconductors-p type

add atoms from *column III* of the periodic table

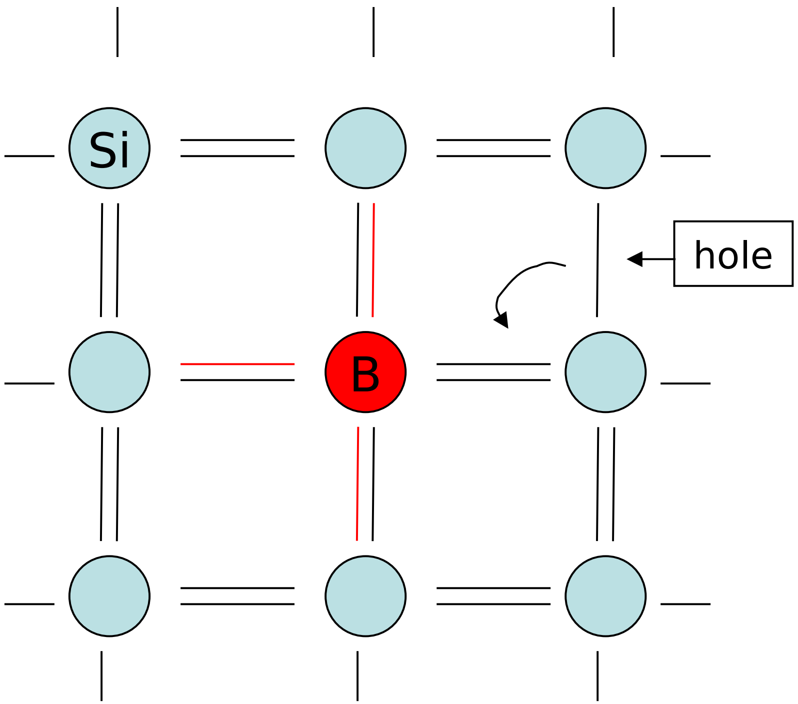


Column III elements have 3 valence electrons that form covalent bonds with Si, but the 4^{th} electron is needed.

This 4^{th} electron is taken from the nearby Si=Si bond.

Extrinsic semiconductors-p type

add atoms from *column III* of the periodic table



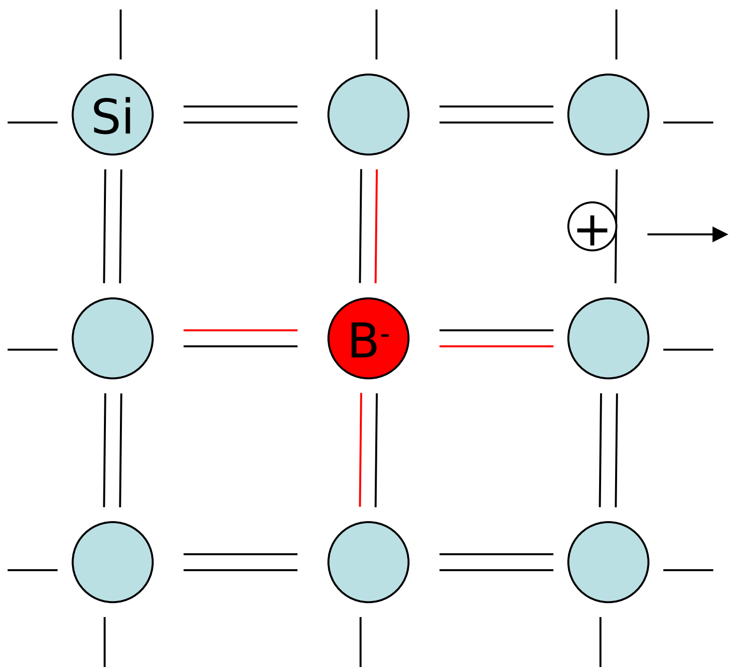
Column III elements have 3 valence electrons that form covalent bonds with Si, but the 4th electron is needed.

This 4th electron is taken from the nearby Si=Si bond.

This “stolen” electron creates a free hole.

Extrinsic semiconductors-p type

add atoms from *column III* of the periodic table



The boron atom has *accepted* an electron from the semiconductor (Column III atoms are called *acceptors*)

The boron has one extra electron, so it has a negative charge (-1)

The boron ion is bound to the silicon, so this -1 charge can't move!

The number of "extra" holes is equal to the number of boron atoms: $p = N_a$

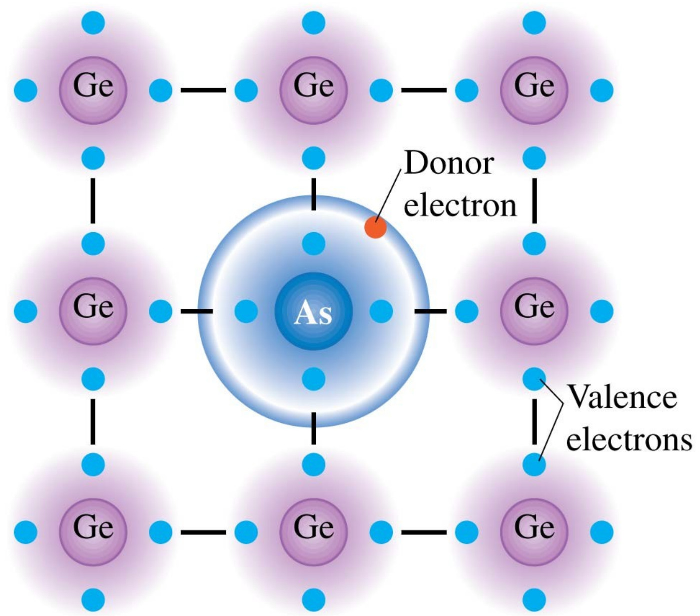
p-type semiconductor (acceptor):

more holes than electrons ($p>n$)

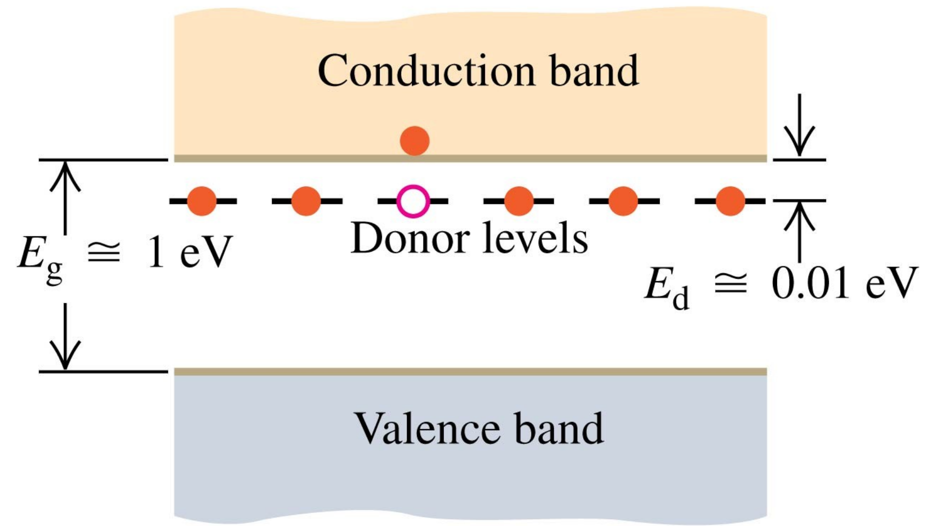
Energy levels with impurities

n-type semiconductor

A donor (n-type) impurity atom has a fifth valence electron that does not participate in the covalent bonding and is very loosely bound.



Energy-band diagram for an n-type semiconductor at a low temperature. One donor electron has been excited from the donor levels into the conduction band.



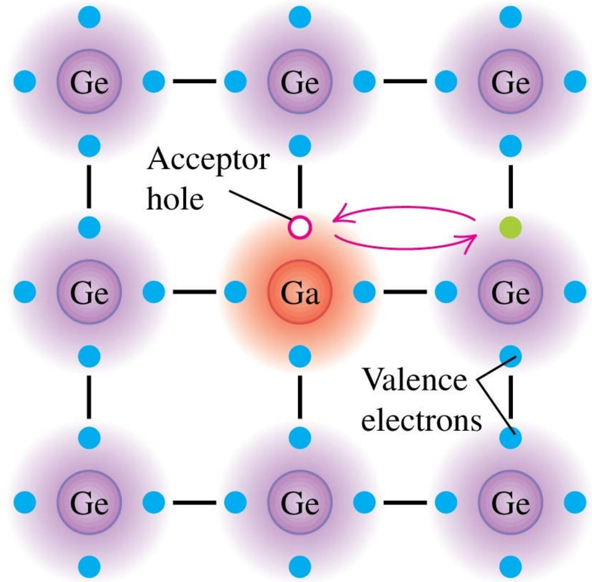
The band structure changes due to the presence of the impurities/doping.

- The donor level of the extra electron from the impurity corresponds to a filled isolated energy level lying in the gap, about 0.01 eV below the bottom of the conduction band. A small amount of energy E_d can excite the electron into the conduction band.
- Resulting conductivity is due almost entirely to negative charge motion (the donated electron). → electrons are the majority and holes the minority carriers

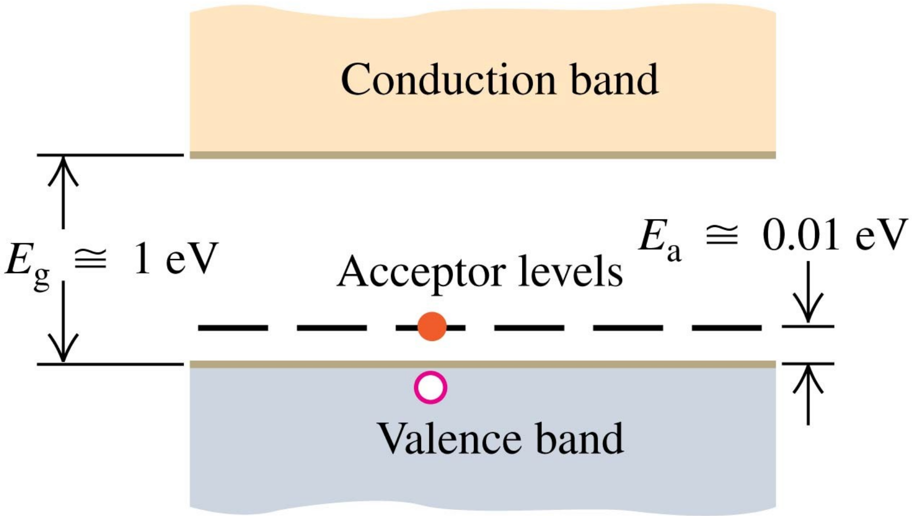
Energy levels with impurities

p-type semiconductor

An acceptor (p-type) impurity atom has only three valence electrons, so it can borrow an electron from a neighboring atom. The resulting hole is free to move about the crystal.



Energy-band diagram for a p-type semiconductor at a low temperature. One acceptor level has accepted an electron from the valence band, leaving a hole behind.



The band structure changes due to the presence of the impurities/doping.

- The acceptor level of the impurity corresponds to an empty isolated energy level lying in the gap, about 0.01 eV above the top of the valence band. A small amount of energy E_a excites an electron into the acceptor energy level leaving a hole in the valence band
- Resulting conductivity is due almost entirely to positive charge motion (hole). → holes are the majority and electrons the minority carriers