Chemistry 2000 Slide Set 7: Band theory of bonding in crystalline solids

Marc R. Roussel

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The free electron model of metals

- Distinguishing properties of metals:
  - High electrical and thermal conductivity
  - Reflective across a wide range of wavelengths (including optical)
  - Ductile and malleable
- One early and surprisingly successful model of metals is the free electron model which assumes that the valence electrons are free to travel throughout the metal.
- Another way to think about it is that the lattice sites are occupied by cations. The valence electrons roam the rest of the space.
- Because the cationic cores are small, we typically treat the metal as an empty box containing electrons, i.e. ignore the cations completely.

Properties explained by the free electron model

High electrical conductivity: Current is carried by the mobile electrons.

High thermal conductivity: Heat can also be carried (in the form of kinetic energy) by the mobile electrons.

Optical properties: Electrons can have a wide range of energies and so can absorb and re-emit at a variety of wavelengths, which makes metals reflective.

Ductility and malleability: Moving atoms relative to each other still leaves each atom surrounded by a sea of electrons, so there is little difference in energy on deformation.

The language of solid-state physics

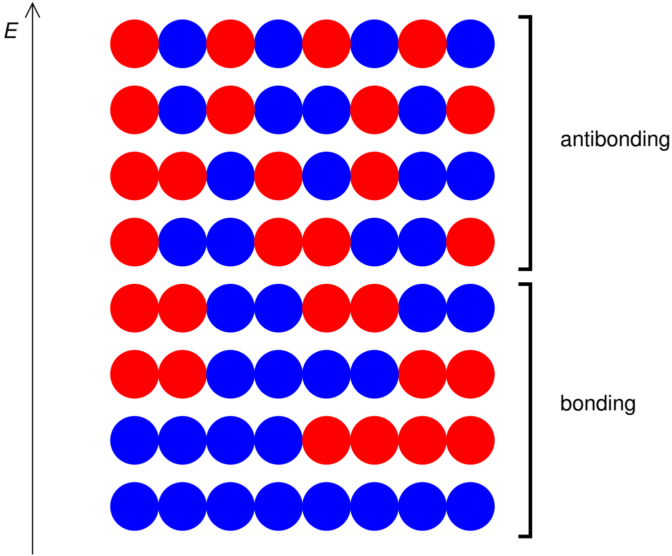
- MO theory and solid-state physics describe the same things using different terminology.
- Translation table:

MO theory	Solid-state physics
Molecular orbital	(Electronic) state
HOMO	Fermi level

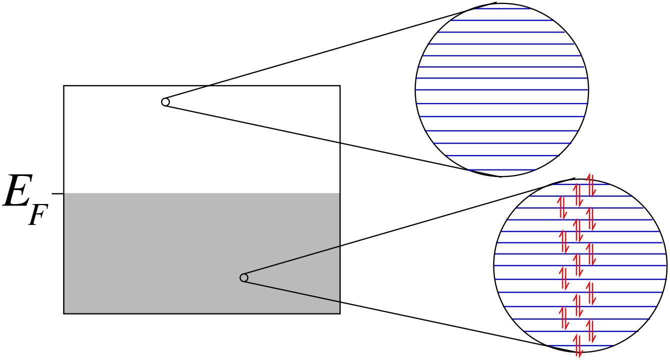
LCAO treatment of crystalline solids

- We can treat bonding in crystalline solids using ideas from LCAO-MO theory.
- If we combine N atomic orbitals, we get N states.
- For real crystals, N is very large so there is a huge number of states.
- As we go up in energy, the states have more and more nodes.
- Each state differs from adjacent states only by a little bit of bonding character, so the energies of adjacent states are very nearly the same.
- Because of this and of the large number of states, the allowed energies effectively form a continuum called a band.

Examples of states in a one-dimensional s band



Occupied and unoccupied states in a band



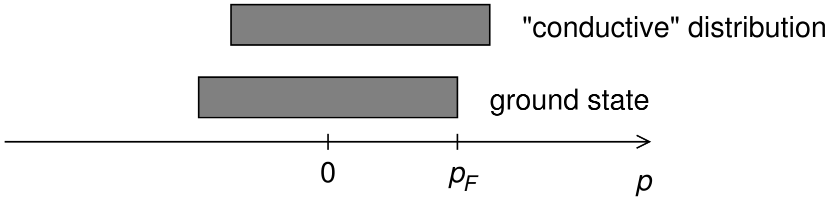
Quantum mechanics of conduction

- In one formulation of quantum mechanics, we describe how the electrons are distributed in momentum space.
- The momentum and energy of an electron are connected.
  For example, in a free electron model, $E = K = p^2/2m$.
- The Fermi level in momentum space is denoted p_F.
- In the ground state, for each occupied momentum p, momentum $-p$ is also occupied.

  On average, the electrons have no momentum, so no current flows.

Quantum mechanics of conduction (continued)

- In order for conduction to occur from left to right (say), we have to shift the electron distribution so that there are more electrons with positive momentum than negative.
  This requires that we take some electrons from the most negative values of p occupied in the ground state and shift them to positive values of p above p_F.

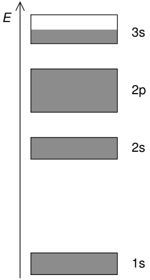


- In terms of energy, this means that we have to shift some electrons to energies above the Fermi level.

Quantum mechanics of conduction (continued)

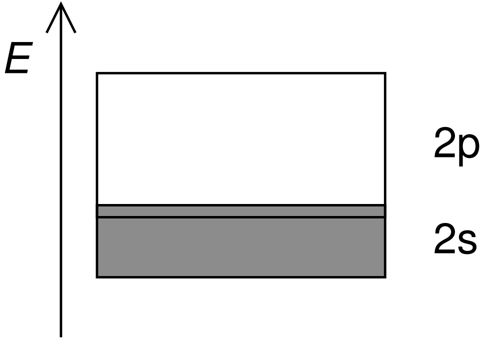
- To shift electrons above the Fermi level, there have to be available states near this level ("near" in the sense of the energy difference not being too much larger than $k_B T$).
- If there are states very near the Fermi level, the material will have metallic conductivity.

Band structure of sodium



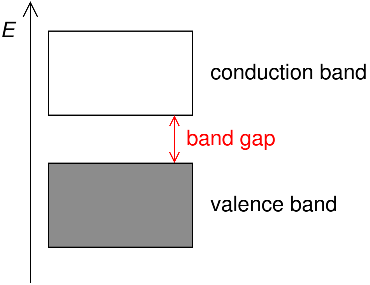
- Note that the 3s (valence) band is half-filled.
    - We have *N* electrons to place in *N* 3s states, but each state can hold 2 electrons.
- Lots of states near the Fermi level ∴ sodium is a conductor.
- As with MOs, the core bands are always filled and do not participate in conduction, so from now on we can ignore them.

Band structure of beryllium



- The 2s band is completely filled, but it overlaps the 2p band.
- Again, lots of states near the Fermi level
  ∴ beryllium is a conductor.

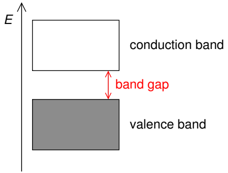
Band structure of diamond



- The 2s and 2p orbitals combine to form two bands separated by a band gap.
- The $4N$ valence electrons completely fill the valence band, which consists of $2N$ states.
- Band gap $\gg k_BT$ $\therefore$ diamond is an insulator.

Measuring band gaps

- Band gaps are measured by absorption spectroscopy.
- The smallest gap between an occupied state and an unoccupied state is the band gap.



- The band gap therefore corresponds to the energy of the lowest frequency (longest wavelength) photon absorbed by the solid.

Band gaps in group 14

Substance	$E_g/(k_B T)$	Resistivity/$\Omega\,\mathrm{m}$	Type
Diamond	2×10^2	$> 10^{11}$	insulator
Si	5×10^1	2.3×10^3	semiconductor
Ge	3×10^1	1	semiconductor
Sn (gray)	3	4×10^{-6}	metal
Pb	0	2.08×10^{-7}	metal

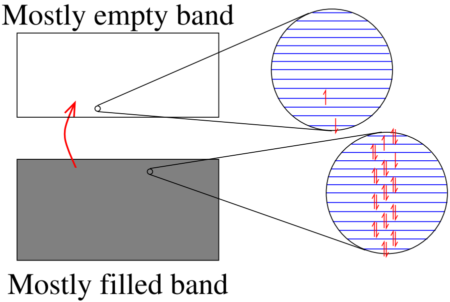
(T near room temperature)

Intrinsic semiconductors

Intrinsic semiconductors have medium-sized band gaps.

- They are moderately good conductors of electricity because a small number of their electrons manage to reach the conduction band.
- Both the electrons in the conduction band and the “holes” left behind in the valence band can carry a current.

Hole conduction in a semiconductor



- The unfilled states in the valence band can be thought of as “holes” in the momentum distribution for electrons in the valence band.
- Because the holes can swap places with an electron, their momentum distribution can also be shifted in response to an electric field.

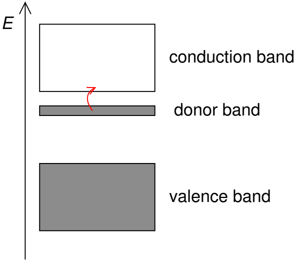
⟹ Holes behave like positive charge carriers.

Extrinsic semiconductors

N-type semiconductors

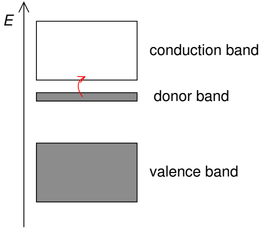
Extrinsic semiconductors have been doped (had impurites added to them) to increase their conductivity.

N-type semiconductors have been doped with an impurity that has more electrons than the host material (e.g. As in Si). The extra electrons can be donated into the conduction band:



Extrinsic semiconductors

N-type semiconductors

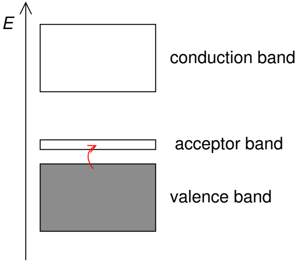


- The dopant is present at very low concentrations, so its atoms are far apart. The donor "band" is analogous to nonbonding orbitals, and electrons cannot travel through it.
- The electrons transferred to the conduction band are the charge carriers.
- The name comes from the negative charge carriers (electrons) in the conduction band.

Extrinsic semiconductors

P-type semiconductors

P-type semiconductors have been doped with an impurity that has fewer electrons than the host material (e.g. Al in Si). This creates a vacant band into which electrons can be donated:



- Name comes from positive charge carriers (holes) in valence band
- Other than creating the holes in the valence band, the acceptor band of the dopant plays no role in conduction.

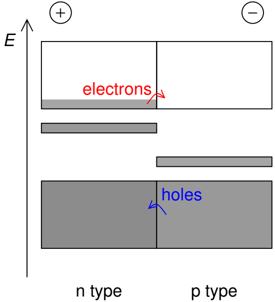
Extrinsic semiconductors

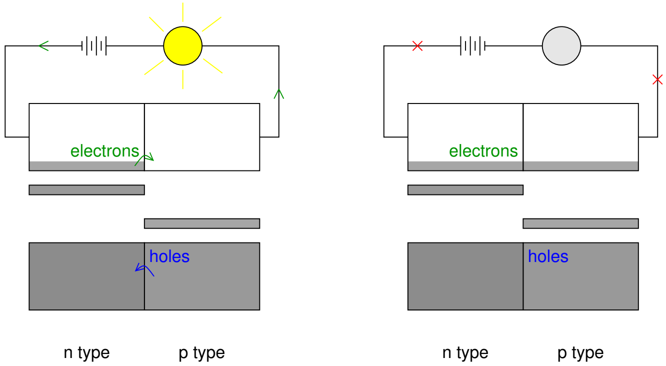
- We have several variables to play with: host semiconductor, dopant, dopant concentration.
- By choosing these variables appropriately, we can achieve very good control over the electrical properties of semiconductors.

Diodes

Diodes are devices that (conceptually) are made by gluing a p-type semiconductor to an n-type semiconductor.

- Negative charge accumulates on the p side until enough electrons and holes have moved to counteract further charge separation.



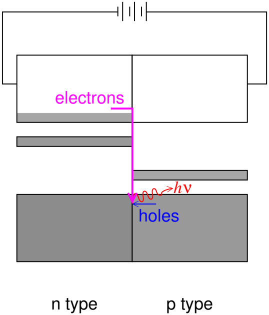


- If we connect the negative terminal of a current source to the n side of the junction and the positive terminal to the p side, electrons will replenish the n side, allowing current to flow.
- If we reverse the connection, electrons will pile up on the p side (provided the voltage applied isn't too large) and no current will flow.

LEDs and solar cells

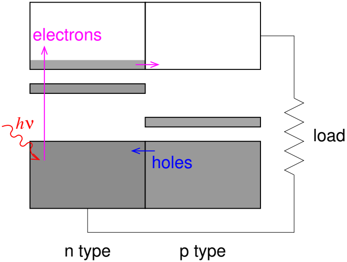
- Next: LEDs and solar cells, both based on diodes
- The devices described below are direct band-gap devices. There are also devices based on indirect band gaps. (The difference is beyond the scope of this course.)
- Advantages of direct band-gap devices:
    - Tend to be more efficient
    - For us: easier to describe
- On the other hand, the properties of indirect band-gap devices are easier to tune by playing with the dopants.

LEDs



- In light-emitting diodes (LEDs), the materials chosen and construction of the device are such that there is a high probability that the electrons will "fall" into holes as they pass through the p-n junction, releasing energy in the form of a photon.
  The color is controlled by the band gap.

Solar cells



- In solar cells, light shining on the n side causes promotion of an electron from the valence band to the conduction band, causing current to flow.