CHEM 1101B- Chemistry for Engineers

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HS (Health Sciences) 1301
Mondays & Wednesdays 8:35am - 9:55am

Lecture 9: Band Theory of Solids

Please feel free to introduce yourself to your neighbors– name, pronouns, a hobby, etc.

and/or

Answer the first question on Wooclap!

Learning outcome for Topic 9: The Molecule – Band Theory

LOs:
•Draw a band diagram for any network solid up to 20Ca
•Predict simple electrical behaviour in network solids


Courtesy of Andy Washnik

Properties of Metals

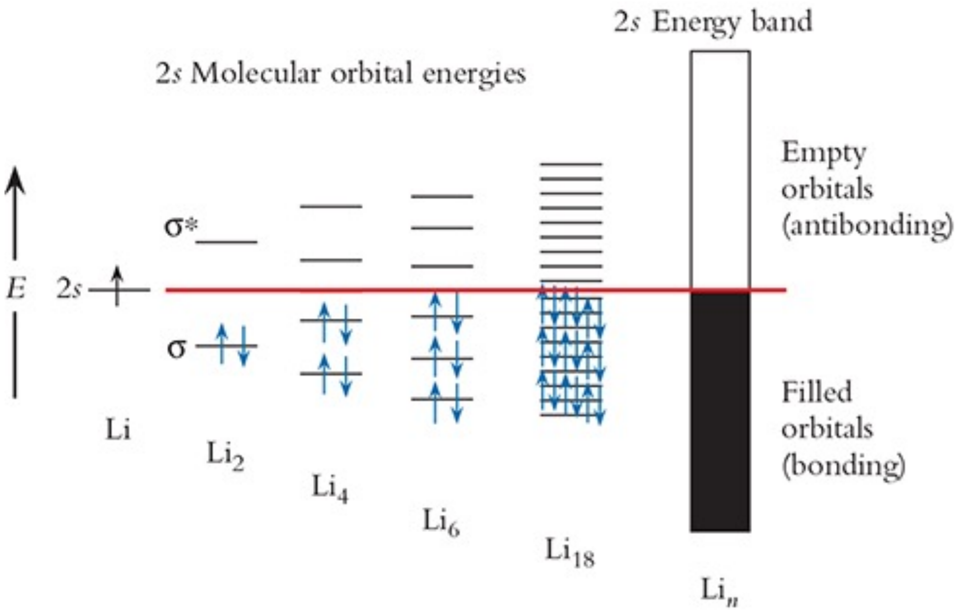
1. Metals and malleable
2. Metals are ductile (drawn into wires)
3. Metals conduct electricity and heat

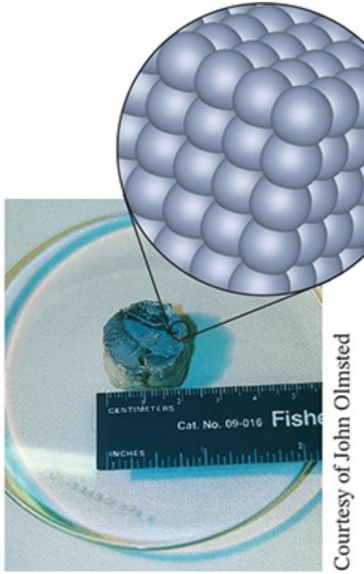
- Properties of metals are consistent with a bonding description that places the valence electrons in delocalized orbitals
- Band theory of solids is an extension of the idea of delocalized orbitals and accounts for properties of metals and metalloids

Band Theory – Delocalized orbitals in lithium metal

Band Theory: The description of bonding in solids using delocalized orbitals

We can consider Li atoms coming together in a cluster one at a time – this develops the idea of “bands”.

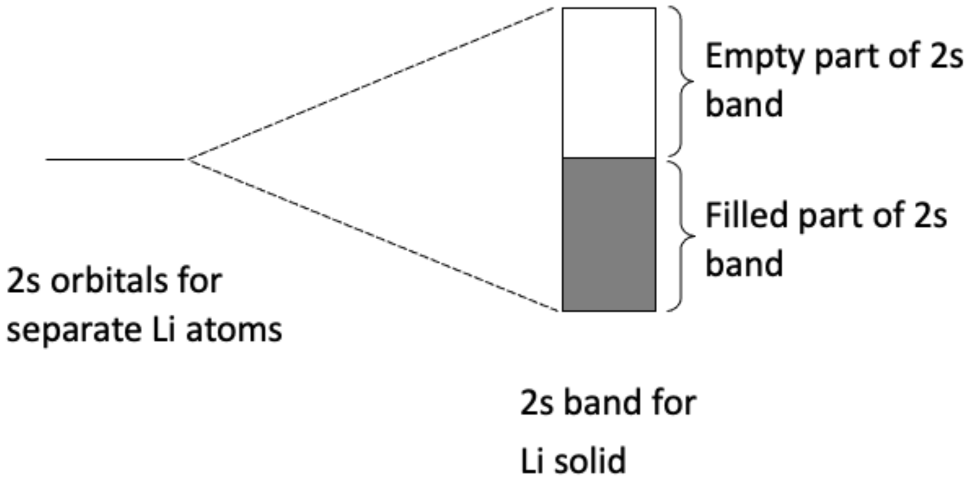




For a solid, N is so large (>10^{20}) that the MO energies form an effectively **continuous band.**

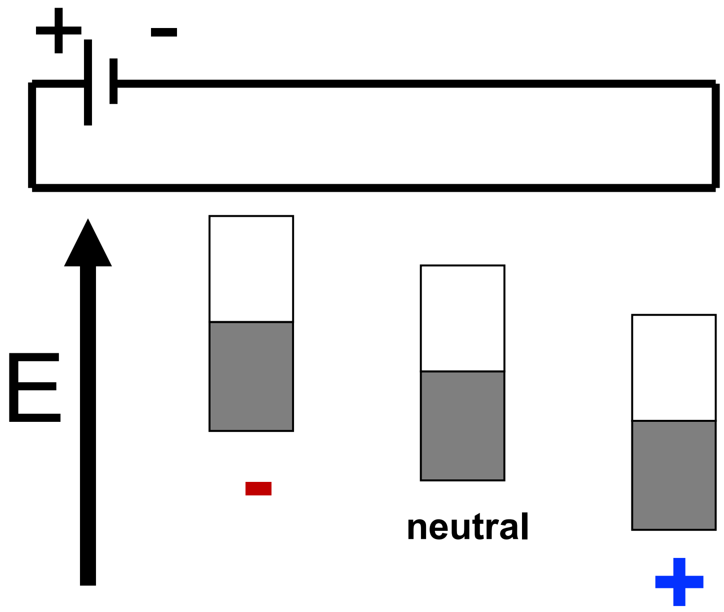
Band Theory – *Why* Lithium conducts electricity

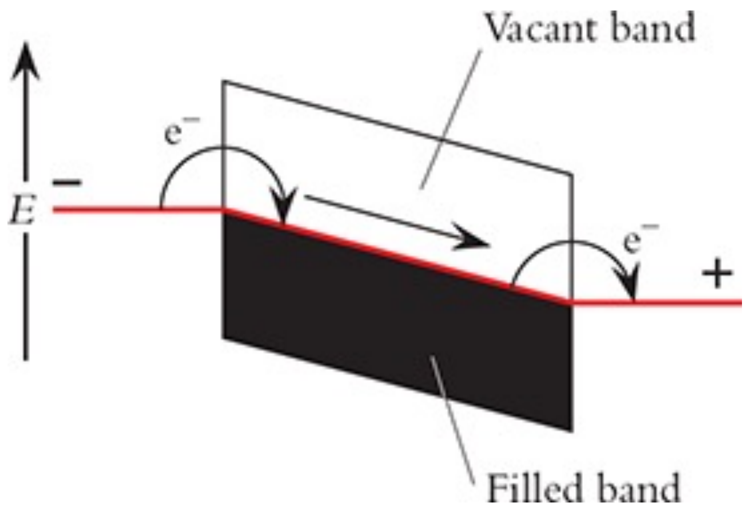
For a solid, N is so large ($>10^{20}$) that the MO energies form an effectively **continuous band.**



- Electrons in the "full" part of the band have empty energy states very close that they can move to (requiring little energy to get there)
- **Allows free movement across physical space, to conduct charge**

Band Theory – Conducting electricity

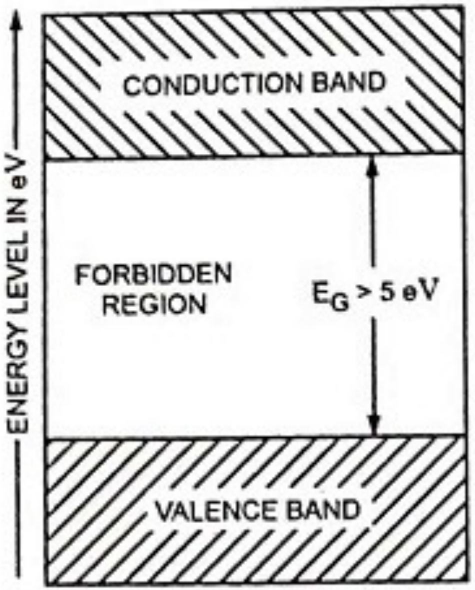




The valence and conduction bands are affected by a potential difference.

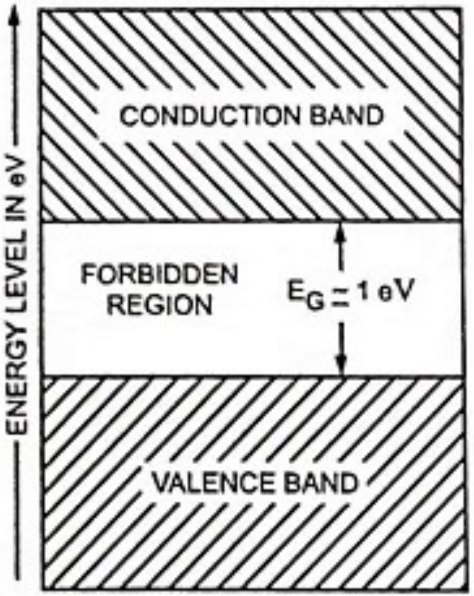
- **Bands close to the negative plate are destabilized through repulsion**
- **Bands closer to the positive plate are stabilized through attraction**
- Electrons flow through the metal from the neg to pos end, generating an **electrical current**

Metals, Insulators and Semiconductors



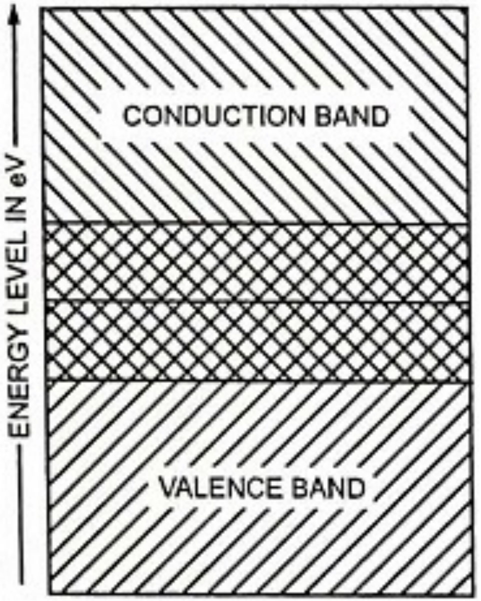
(a) Insulator

No charge transfer



(b) Semiconductor

Sometimes a charge transfer (depends on conditions)



(c) Metal

Always a charge transfer

Insulators and Conductors: Carbon vs. Lead

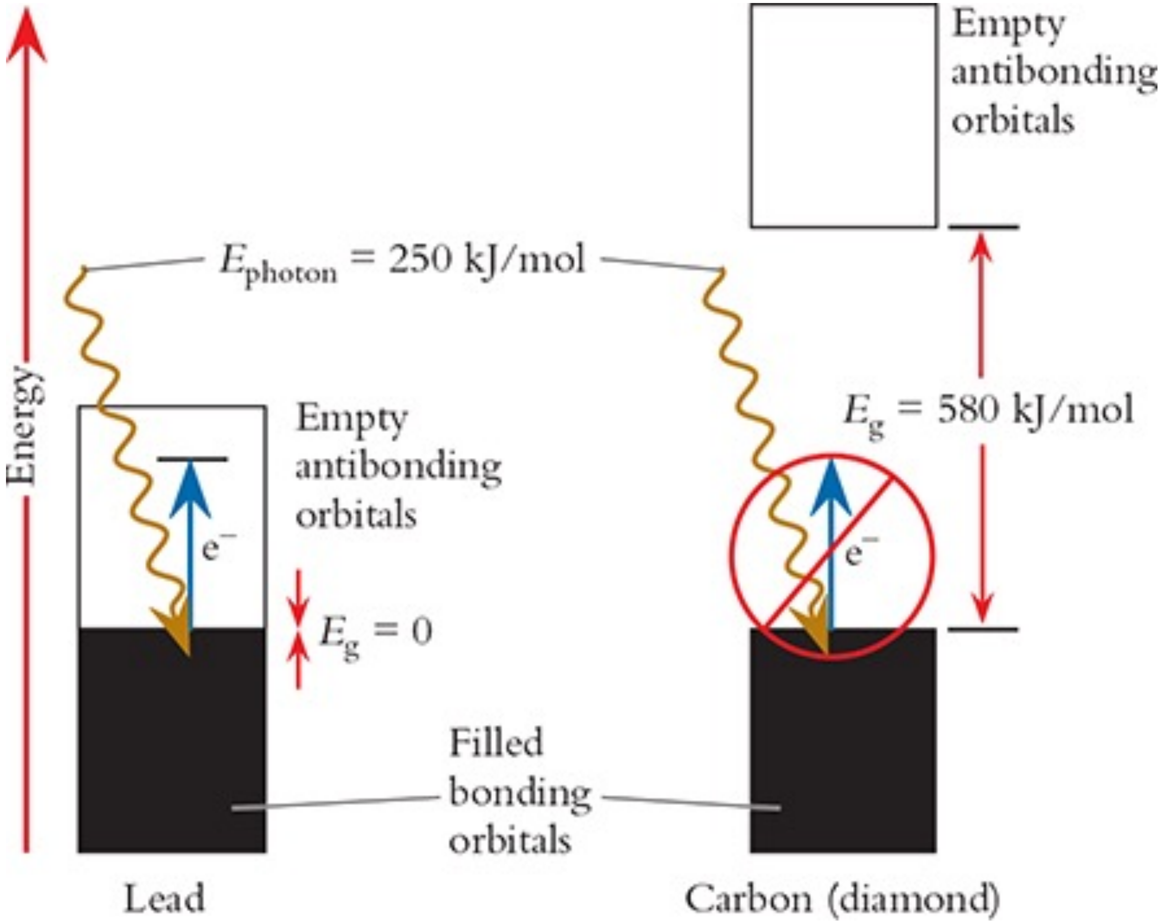
Metallic lead is dark in colour and is an **electrical conductor** (a substance that is a good conductor of electrical current).

Diamond, the most valuable form of carbon, is transparent and is an **electrical insulator**.

If both Lead and Carbon are in Group 14 of the periodic table and have the same valence configuration, **make a hypothesis why diamonds are transparent insulators, whereas lead is a dark-coloured conductor?**

Insulators and Conductors: Carbon vs. Lead

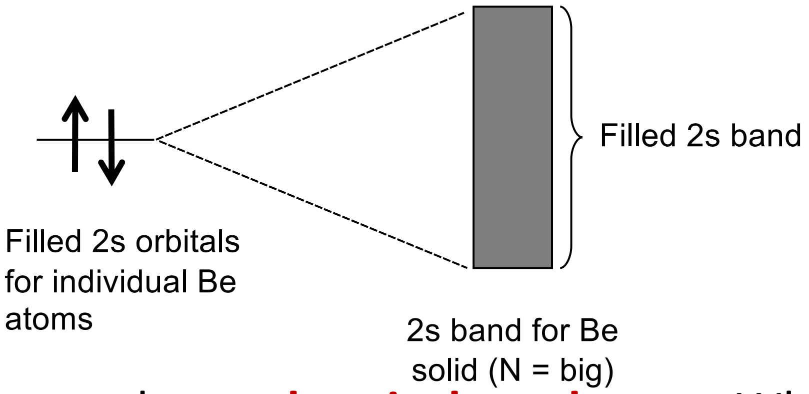
- Electrons can be promoted into the conduction band through light or heat
- Materials with **large band gaps** prevent this – **called insulators**
- Materials with **small or no band gaps** enable this **– called conductors**
  - Metals (e.g., Lead) conduct heat and electricity because their band gaps are small



Does Beryllium conduct electricity?

Electrons in completely filled bands can't be moved by electric fields, and therefore are poor electrical conductors.

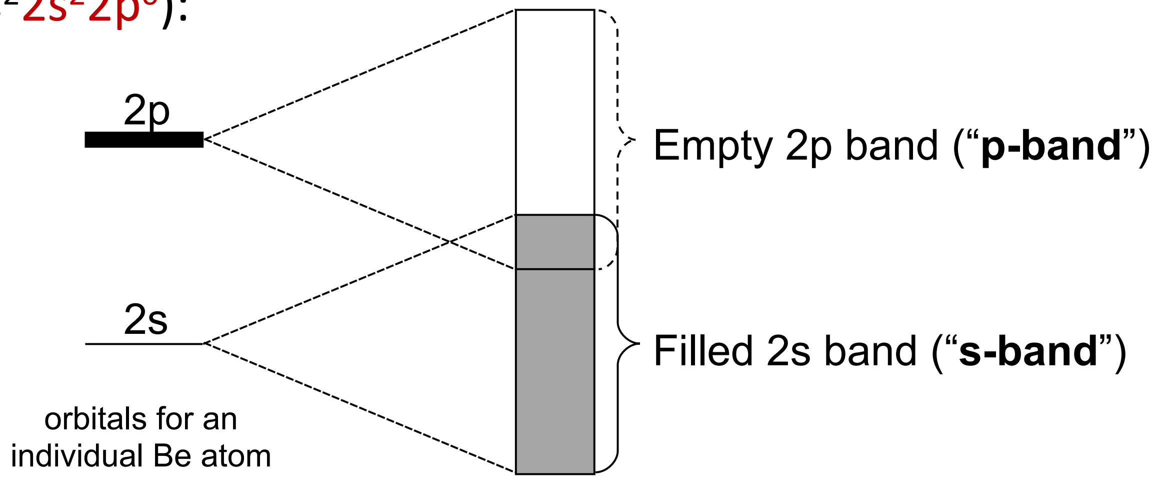
Beryllium has 2 valence electrons per atom, just enough to completely fill the 2s band (unlike Li), so Be **should be** an electrical *insulator*.



But! Be metal is, famously, an **electrical conductor**. Where did the theory go wrong?

Beryllium conducts electricity!

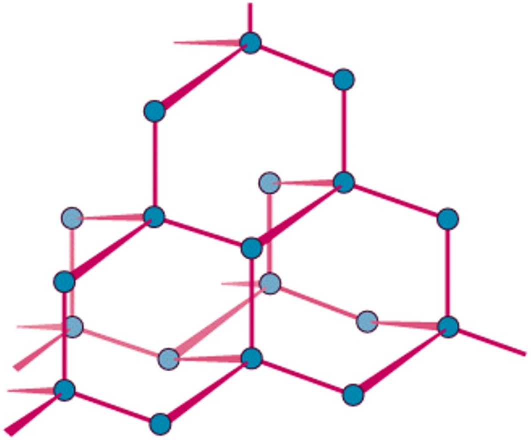
Instead, we must consider **both** 2s and 2p (valence) molecular orbitals for beryllium atoms ($1s^2 2s^2 2p^0$):

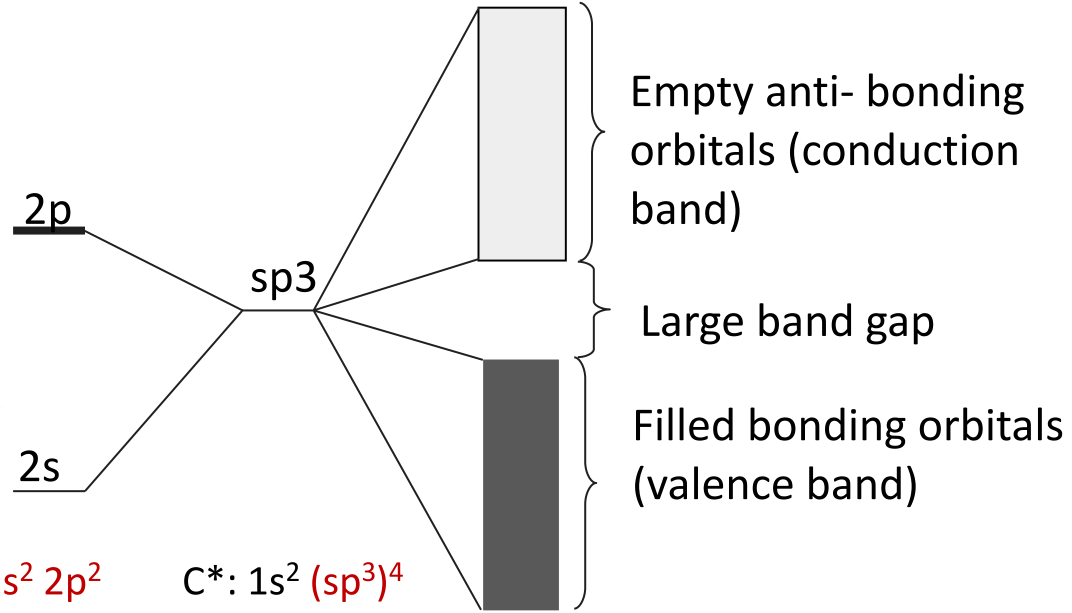


- Overlapping 2s and 2p bands form a **single band** that is **partially filled**.
- Be metal is an electrical conductor because the electrons now have somewhere nearby to go.

Why does diamond (carbon) not conduct electricity?

- Carbon has 4 valence electrons per atom, enough to half-fill 2s+2p bands, so diamond should be an electrical conductor.
- However, diamond has a structure where every carbon is tetrahedral sp^3.
- There is just enough electrons to fill valence band (bonding orbitals), giving an **insulator**.





C: $1s^2$ $2s^2$ $2p^2$ C*: $1s^2$ $(sp^3)^4$

Practice: Drawing band diagrams

Draw and label the band diagram for:

a) Mg_2 (*Mg: $1s^2\ 2s^2\ 2p^6\ 3s^2$*)

b) Mg_N (*Mg: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^0$*)

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Is there a band gap in Mg_N ?

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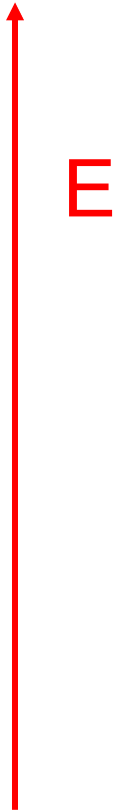
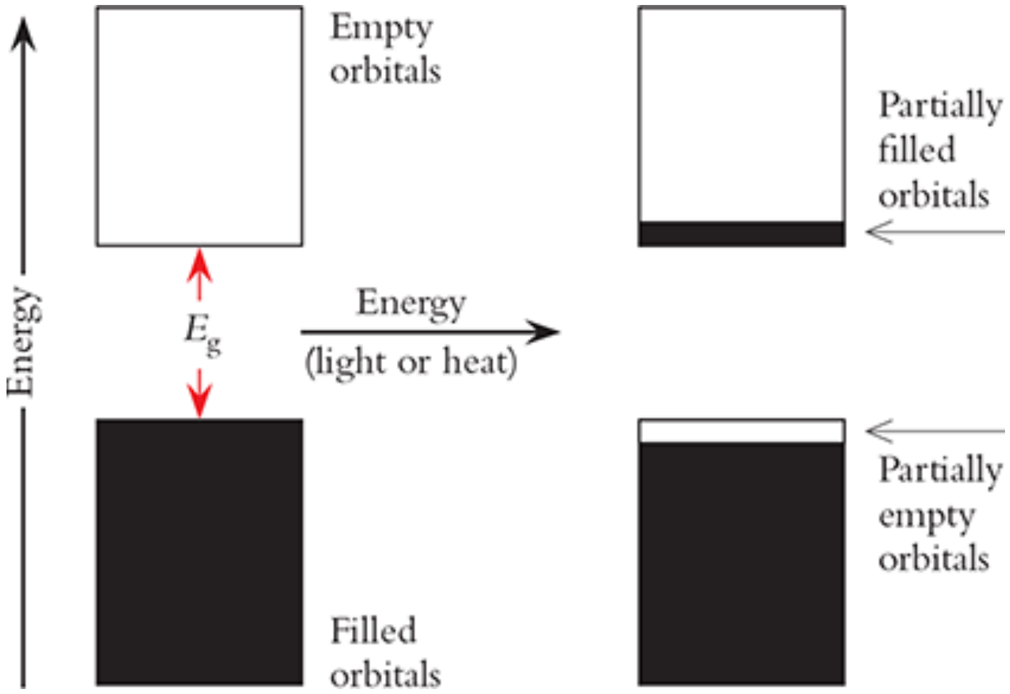
Practice: Drawing band diagrams

Draw and label the band diagram for $\mathbf{Al_N}$



Metalloids

Metalloid: an element with properties intermediate between those of metals and non-metals (e.g., silicon and germanium)



- When electrons are transferred into the high-energy conduction band, they can move freely among the vacant orbitals of the band
- Electron transfer creates **vacancies (holes)** among the bonding orbitals in the low energy band
- **Holes and high-energy electrons allow electricity to flow**

Example: Intrinsic Semiconductors

CdS, a semiconductor studied for use in solar cells, absorbs blue light at 470 nm.

Calculate its band gap in kJ/mol

$$E_{photon} = E_{gap} = \frac{h \cdot c}{\lambda}$$

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Example: Properties of Photoconductors

Electric eye" door openers use photoconductors that respond to infrared light with a wavelength of 1.5 μm . **Which is suitable for photoconductors operating at this wavelength: germanium (E_g= 64 kJ/mol) or silicon (E_g= 105 kJ/mol) ?**

1μm = 10^{-6} m

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Doped (extrinsic) Semiconductors

Doped Semiconductors:

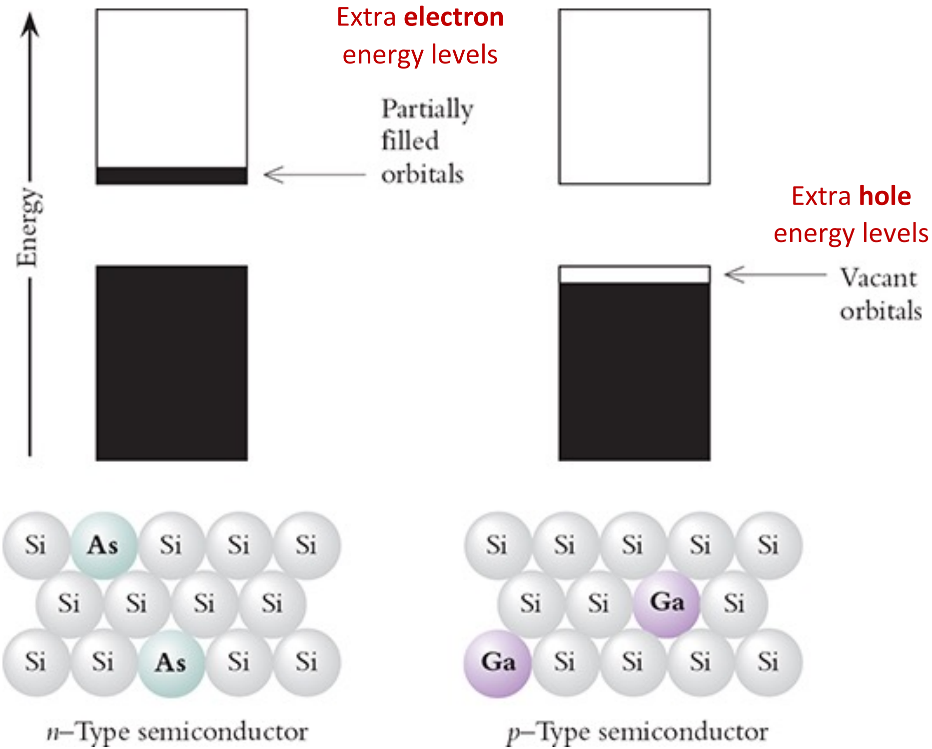
- A metalloid to which a small amount of another element has been added
- Has almost the same band structure as the pure material, but it has different electron populations in its bands

N-type semiconductor

- Metalloid that contains a dopant that gives it **excess valence electrons**

P-type semiconductor

- Metalloid that contains a dopant that gives it a **deficiency of valence electrons**



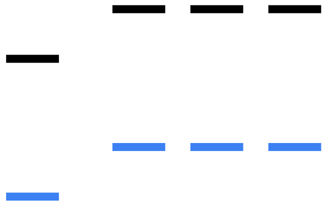
Practice: Constructing *n*-type semiconductors

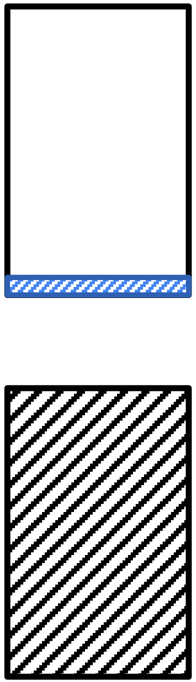
Si_NAs_n N is a large number

n<<N (and right now, n=1)

Si: *[Ne]* *3s²* *3p²*

As: *[Ar]* ***4s²*** 3d¹⁰ ***4p³***





N x Si*: ( )

1 x As*: ( )

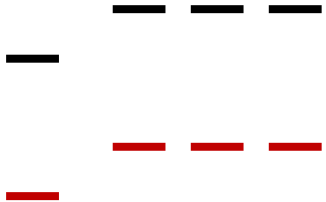
Practice: Constructing *p*-type semiconductors

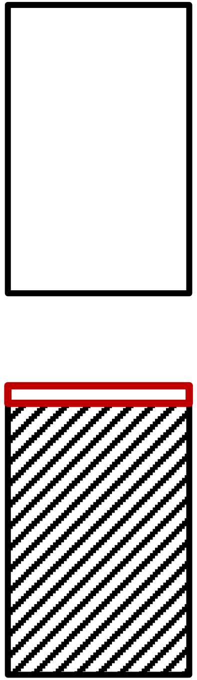
$Si_N Ga_n$ N is a large number

Si: *[Ne]* ***3s²*** ***3p²***

n<<N (and right now, n=1)

Ga: *[Ar]* ***4s²*** 3d¹⁰ ***4p¹***





N x Si*: ( )

1 x Ga*: ( )

Example: Mixed Instrinsic Semiconductors

Draw a band-gap diagram that illustrates a semiconductor made of gallium arsenide (50:50 mixture).

$Ga_{N/2}As_{N/2}$ (N is a large number)

Ga: *[Ar]* ***4s***^{2} *3d*^{10} ***4p***^{1}

As: *[Ar]* ***4s***^{2} *3d*^{10} ***4p***^{3}

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When drawing a semiconductor band diagram, we draw:

a) No band gap
b) Small band gap
c) Large band gap

Example: Doped (Extrinsic) Semiconductors

Draw a band-gap diagram that illustrates a semiconductor made of gallium arsenide (50:50 mixture) **doped with zinc atoms.** $Ga_{N/2}As_{N/2}$ (N is a large number)

Ga: *[Ar]* ***4s²*** *3d¹⁰* ***4p¹*** — — — —

As: *[Ar]* ***4s²*** *3d¹⁰* ***4p³*** — — — —

Example: Designing semiconductors

You have been asked to develop a p-type semiconductor using Al, Si, and/or P. Which **two elements would you choose**, and **what role would each element play in the semiconductor?**

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Chemistry and Technology: Light- emitting diodes

- A modern application of solid-state electronic devices is semiconductor materials that convert electrical energy into light
- Light-emitting diodes (LEDs) are used for visual displaying and solid-state lasers
- Heart of a LED is a junction between a p-type and n-type semiconductor

Alan Marsh/Alamy Stock Photo