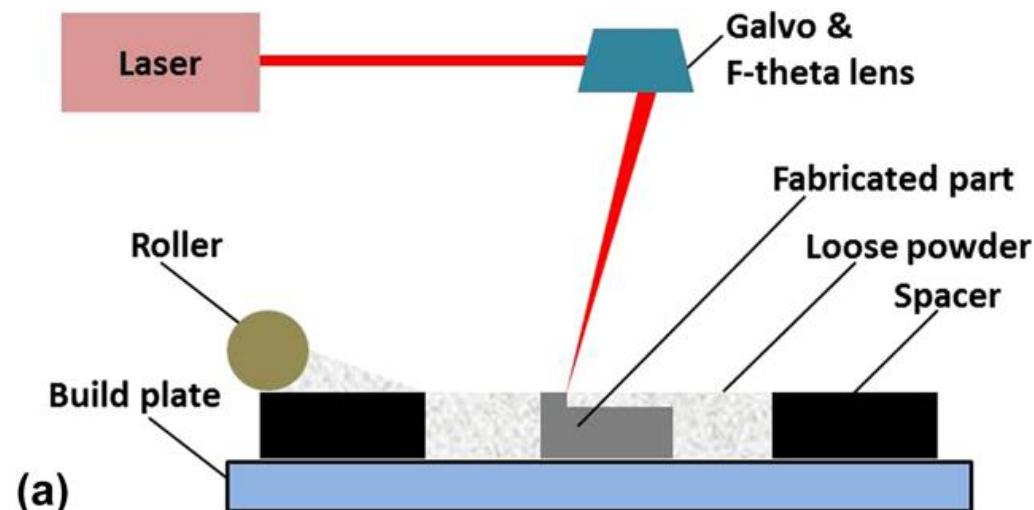


# Thermoelectric (TE) technologies and devices

- Emerging fabrication techniques based on printing: laser printing

Laser additive manufacturing of powdered bismuth telluride, *J. Mater. Res.* 33 (2018) 4031–4039.



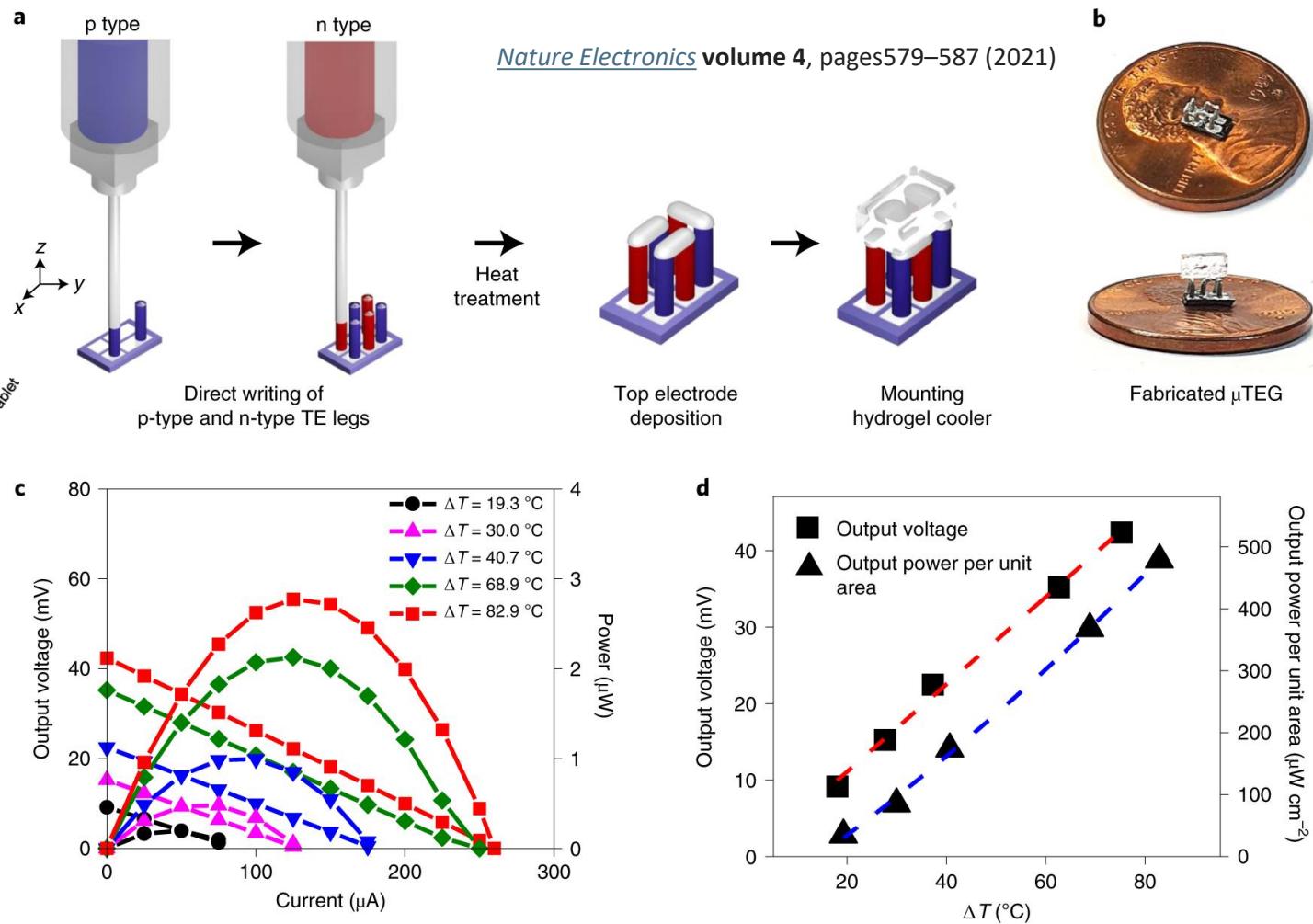
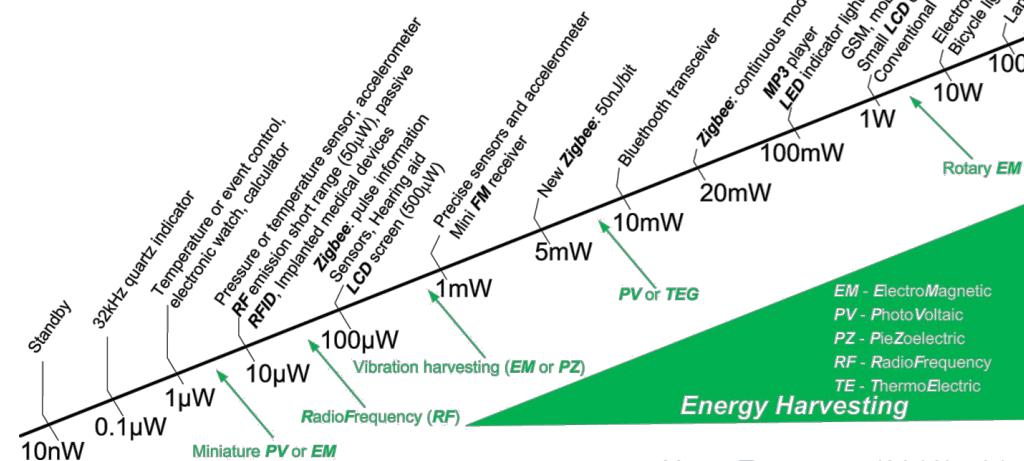
$\text{Bi}_2\text{Te}_3$  –based, moderate  $zT < 0.15$



# Thermoelectric (TE) technologies and devices

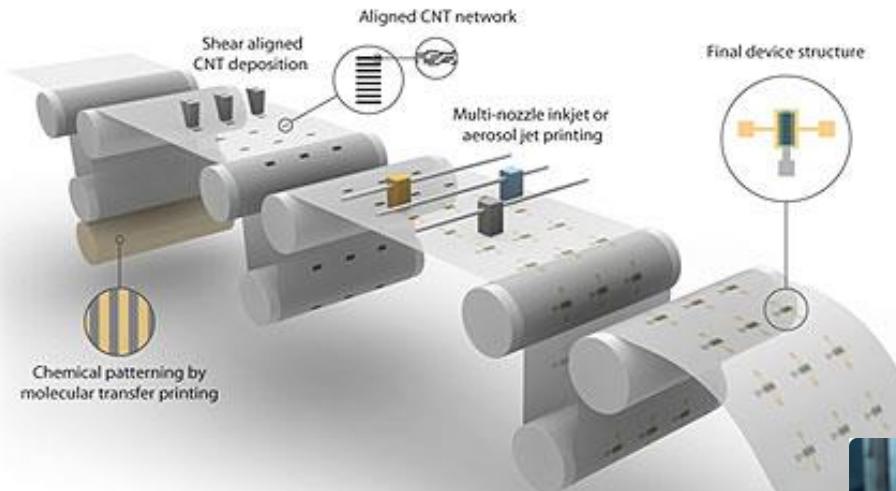
- Emerging fabrication techniques based on printing: microextrusion or direct ink writing (DIW).

Micro devices based on  $\text{Bi}_2\text{Te}_3$  can be printed offering few 100s of micro watts per  $\text{cm}^2$  for  $\Delta T$  of 10's K.



# Thermoelectric (TE) technologies and devices

- **Flexible and printed thermoelectrics** for wearables are mostly based on organic materials that can be printed from liquid phase.

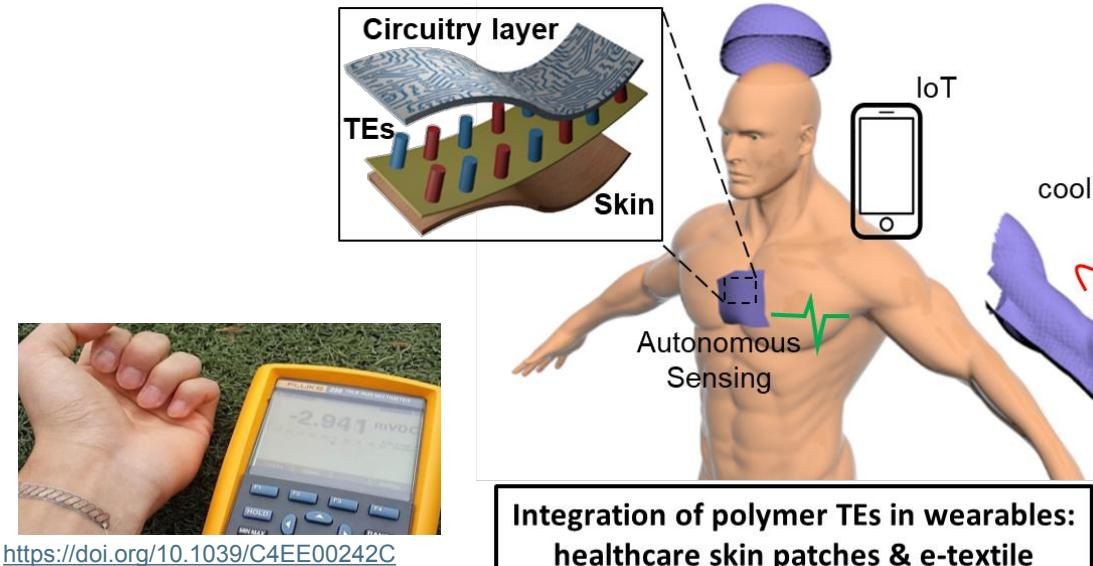
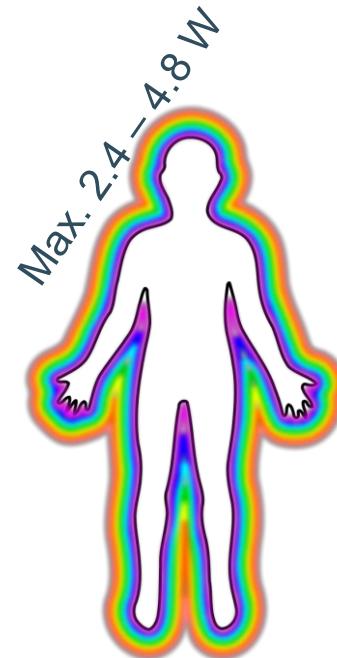


<http://muri-printed-electronics.umn.edu/>



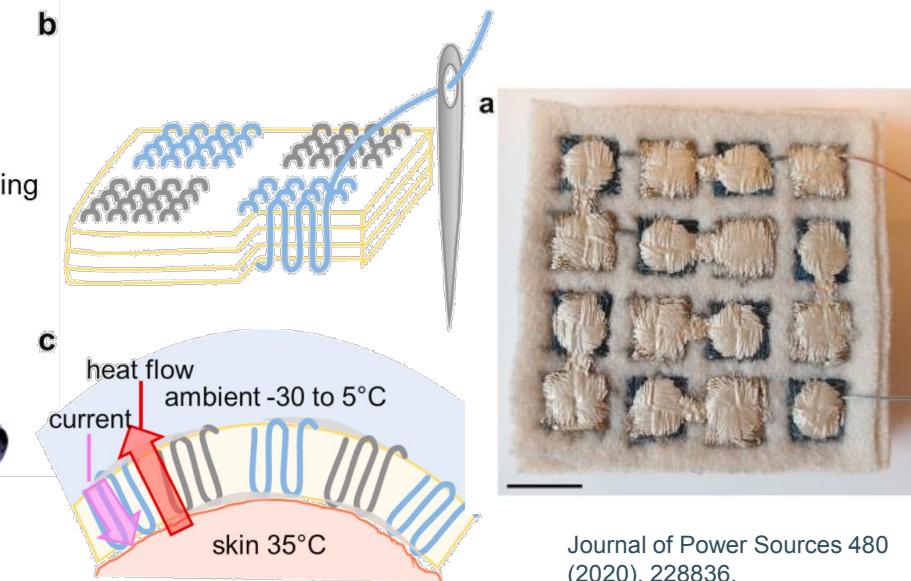
# Thermoelectric (TE) technologies and devices

- Flexible and printed thermoelectrics for wearables: energy harvesters



<https://doi.org/10.1039/C4EE00242C>

Integration of polymer TEs in wearables:  
healthcare skin patches & e-textile



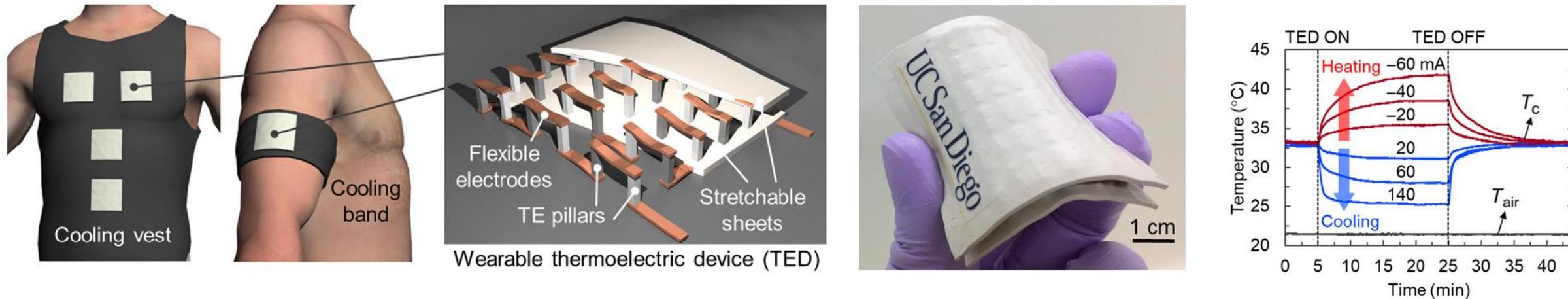
Journal of Power Sources 480  
(2020), 228836.

T. Starner, J.A. Paradiso, Human Generated Power for Mobile Electronics, *Low-Power Electronics Design*, Boca Raton (2004), pp. 1-35

# Thermoelectric (TE) technologies and devices

- Flexible and printed thermoelectrics for wearables: Flexible coolers for body thermal regulation

Hong et al., Sci. Adv. 2019;5 : eaaw0536 17



Flexible thermoelectric device (TED) based on rigid  $\text{Bi}_2\text{Te}_3$  rigid pillars that can deliver more than 10°C cooling effect with a high coefficient of performance (COP > 1.5).

# Materials Physics and Technology for Nanoelectronics



**Clement Merckling**  
[clement.merckling@kuleuven.be](mailto:clement.merckling@kuleuven.be)  
imec & KU Leuven (MTM)  
Kapeldreef 75, B-3001 Leuven



**Francisco Molina-Lopez**  
[francisco.molinalopez@kuleuven.be](mailto:francisco.molinalopez@kuleuven.be)  
MTM Functional Materials  
Kasteelpark Arenberg 44, B-3001 Leuven

# Materials Physics and Technology for Nanoelectronics

## Magnetic materials



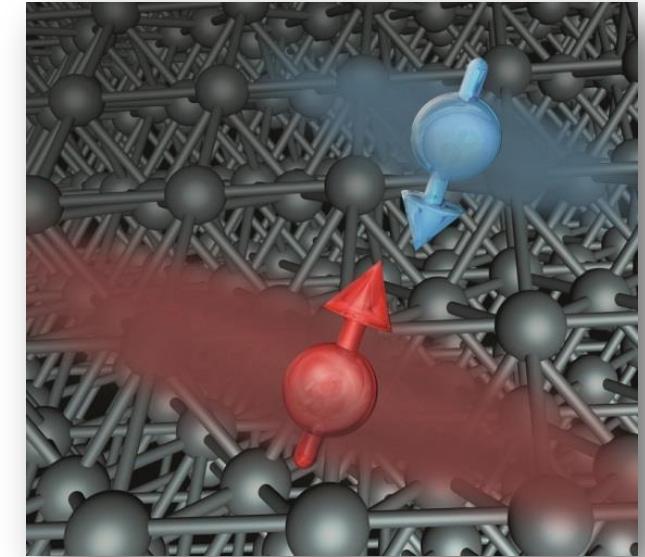
**Clement Merckling**  
[clement.merckling@kuleuven.be](mailto:clement.merckling@kuleuven.be)  
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**Francisco Molina Lopez**  
[francisco.molinalopez@kuleuven.be](mailto:francisco.molinalopez@kuleuven.be)  
MTM Functional Materials  
Kasteelpark Arenberg 44, B-3001 Leuven

# Outline

- Magnetism
- Magnetic materials
- Magnetic anisotropy & domains
- Spin transport
- Giant magnetoresistance
- Spin polarized devices
  - Hard Disk Drive (HDD) based on GMR
  - Magnetic Tunnel Junction (MTJ) and Magnetic RAM (MRAM)
  - Spin Transfer Torque (STT) and STT MRAM



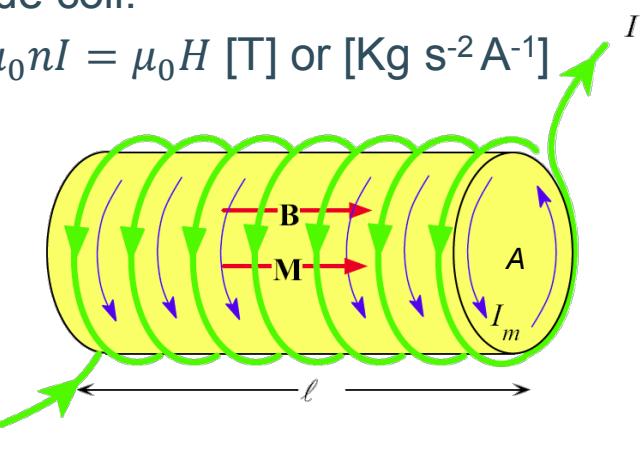
# Magnetism



# Magnetism

- All conductors respond to changing magnetic fields, because via Faraday's law of induction, changing magnetic fields induce electrical fields. In contrast most materials have little response to steady magnetic fields, they are essentially nonmagnetic. The few materials that are magnetic are very important for memories.
- The **inductors** can be seen as the magnetic equivalent of capacitors. While capacitors store their energy in an electric field, inductors can store energy in a **magnetic field**.
- The simplest form of an inductor consists of a coiled conductor.

- An empty inductor is characterized as follows:
  - Magnetic field inside coil:

$$B = \mu_0 n I = \mu_0 H \text{ [T] or [Kg s}^{-2}\text{A}^{-1}\text{]}$$


with  $\mu_0$  being the magnetic permeability in [H/m] (*Henries per meter*) or [ $N/A^2$ ],  $n$  is the number of turns of the coil per length [ $m^{-1}$ ], and  $I$  is the electrical current in the coil in [A].

- The **inductance**  $L = \mu_0 n^2 A l$  incorporates the dimensions of the inductor. The units for  $L$  is [H].

# Magnetism

- Inserting a magnetic material within the coils of the inductor increases its inductance, and its stored energy, by the factor  $\mu_r$ , the **relative permeability**. The magnetic field has now two parts, a contribution from the **current** through the coil (an applied field) and a contribution from the **material**:

$$B = \mu_0 nI + \mu_0 M = \mu_0 H + \mu_0 M = \mu_0 \mu_r H$$

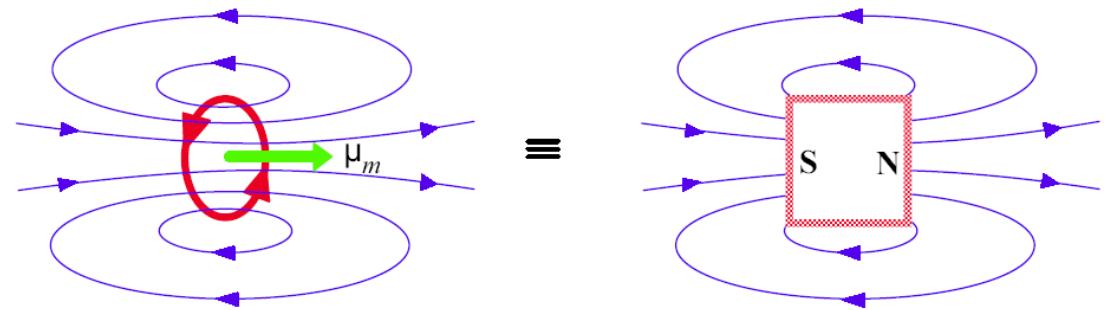
- $B$  represents the **total magnetic field** (or magnetic induction),  $H$  is the **magnetizing field** (or magnetic field strength) [A/m] and  $M$  is the **magnetization** [A/m] due to the material and equals the net magnetic dipole moment per unit volume.
- The relative permeability  $\mu_r$  of the material represents the ratio of the total field in the material to the applied field:
$$\mu_r = \frac{B}{\mu_0 H} = 1 + \frac{M}{H} = 1 + \chi_m$$
- where  $\chi_m$  is the (unitless) **magnetic susceptibility**.

# Magnetism

- Magnetic susceptibility  $\chi_m$  is thus a dimensionless proportionality constant that indicates the **degree of magnetization** of a material in response to an applied magnetic field. The susceptibility indicates whether a material is attracted ( $>0$ ) into or repelled ( $<0$ ) out of a magnetic field, which in turn has implications for practical applications.
- The magnetic susceptibility  $\chi_m$  of most solids is close to 0 and typically falls between  $-10^{-5}$  and  $+10^{-3}$ , meaning  $\mu_r$  is close to 1.
- Materials with small positive magnetic susceptibilities are called **paramagnetic**, and those with small negative magnetic susceptibilities are called **diamagnetic**. For most practical purposes, they can be considered **non-magnetic**.
- A few materials have magnetic susceptibilities of many thousands and their magnetization can vary non-linearly with applied field, that is  $M$  can vary **non-linearly** with  $H$ .

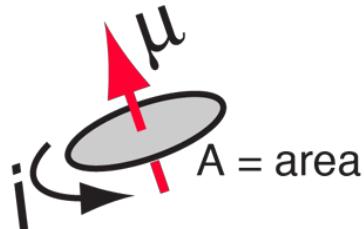
# Magnetic dipoles

- Although electric and magnetic fields, as described by Maxwell's equations, are formally very similar, there is a striking asymmetry between electricity and magnetism in nature, associated with the apparent non-existence of elementary magnetic charges (*i.e.* magnetic monopoles) and magnetic current.
- There are, however, what appear to be **magnetic dipoles**, analogous to electric dipoles.
- A magnetic dipole is a system which when placed in an external magnetic field, experiences a **torque** that tries to rotate the system so as to align its axis parallel to the magnetic field.
- The most familiar example of a magnetic dipole is a bar magnet. The external magnetic field produced by a circular loop of current is identical to that produced by a point magnetic dipole, so the current loop is also a dipole.



# Magnetic dipoles

- The magnetic dipole is characterized by its **magnetic dipole moment**. Let's for example look into the magnetic dipole moment of a current carrying coil (magnetic dipole) of area  $A$ .



- A magnetic moment is created defined by a vector  $\mu = IA$ , where  $I$  is the current through the coil and  $A$  is the area enclosed by the current coil.
- The torque is given by:  $\vec{T} = \vec{\mu} \times \vec{B}$ . This torque tends to line up the magnetic moment with the magnetic field  $B$ , so this represents its lowest energy configuration  $E = -\vec{\mu} \cdot \vec{B}$ .

- The magnetic effect in magnetic materials are due to atomic magnetic dipoles in the materials. The sources that contribute to atomic magnetic moments are:

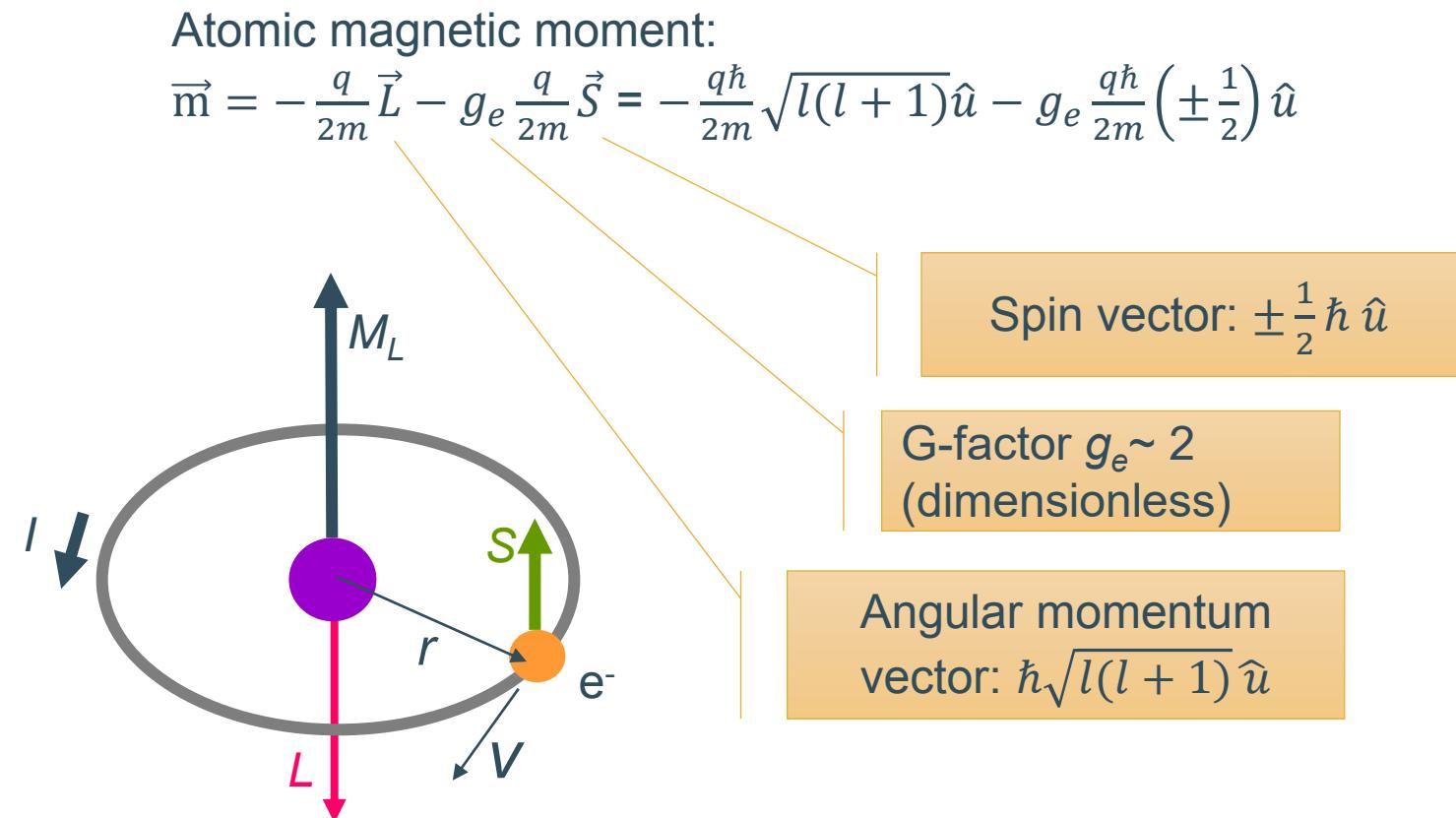
- The electrons “orbiting” around the nucleus in an atom behave like a current loop and have a magnetic dipole moment associated with it, called the **orbital magnetic moment**.
- The magnetic moment due to spin of an electron, i.e. due to spin angular momentum, is called the **spin magnetic moment**.
- In addition, there can be a small contribution from the nucleus called **nuclear magnetic moment**. This effect is usually not significant.

# Magnetic moment

- The total magnetic moment of an electron is given by the sum of the orbital magnetic moment and the spin magnetic moment.
- The **Bohr magneton** is a physical constant and the natural unit for expressing the magnetic moment of an electron caused by its orbital or spin angular momentum.

Bohr magneton:

$$\mu_B = \frac{q\hbar}{2m} = 9.28 \times 10^{-24} [\text{A m}^2] \text{ or } [\text{J T}^{-1}]$$



# Orbital magnetic dipole moments (extra)

- Consider an electron moving with velocity ( $v$ ) in a circular Bohr orbit of radius  $r$ . It produces a current:

$$i = -\frac{q}{T} = -\frac{q\omega}{2\pi}$$

where  $T$  is the orbital period of the electron.

- The current loop produces a magnetic field, with a moment  $\mu_l$ :

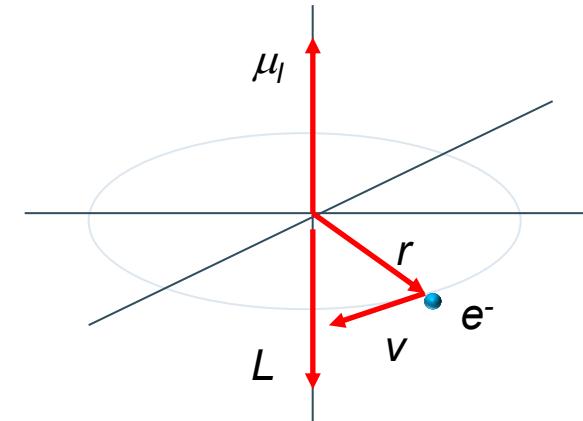
$$\mu_l = iA = -\frac{q\omega}{2\pi}\pi r^2 = -\frac{1}{2}q\omega r^2$$

- The magnitude of orbital angular momentum is  $L = mvr = m\omega r^2$ .
- Combining with previous equation yields:

$$\mu_l = -\frac{q}{2m}L \text{ (see previous slide)}$$

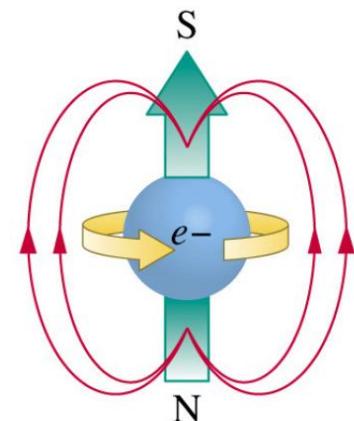
- Electron in external magnetic field  $\vec{B}$  along the axis  $z$ :  $\vec{B}$  creates a torque that aligns  $\vec{\mu}_l$  with  $\vec{B}$ . Quantum theory postulates that the projection of  $L$  on an axis (let's assume  $z$ ) is  $L_z = m_l\hbar$ . The minimum magnetic moment corresponds to  $L_z = \hbar$ , and :

$$\mu_B = \frac{q}{2m}\hbar = 9.27 \times 10^{-24} \text{ Am}^2 \quad (\text{Bohr magneton})$$

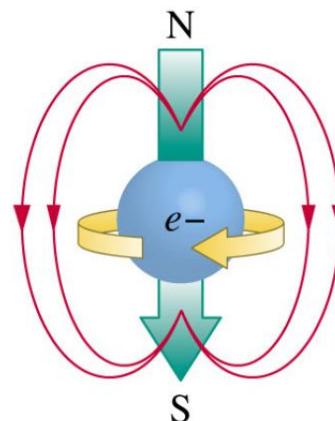


# Electron spin

- As well as mass and charge, an electron has another intrinsic property, i.e. spin angular momentum, or simply **spin**.
  - In quantum mechanics, spin is a fundamental property of atomic nuclei and elementary particles and is an important intrinsic **degree of freedom**.
  - Although as the name indicates spin was originally thought of particles spinning around their own axis, it had been shown by Dirac that electron spin arises naturally within relativistic quantum mechanics.
  - The component of **electron spin** measured along any direction can only take on the values:
- $\hbar s_z$  with  $s_z = \pm \frac{1}{2}$
- Namely, in a classical picture, electron spin can only point to **up or down** along a magnetic field which can be vividly illustrated by a small magnet with its north pole pointing to up or down as shown in the figure.



$$s_z = +\frac{1}{2}$$



$$s_z = -\frac{1}{2}$$

*Classical illustration of electron spin as a small magnet with north pole pointing to up or down.*

# Magnetic materials



# Hund's rule

- In order to understand the magnetic properties of materials, we have to take a deeper look into the **electrons spin distribution**. Each electron state may be occupied by two electrons, one with spin up and one with spin down. The electron spin distribution is determined by **Hund's rule**.

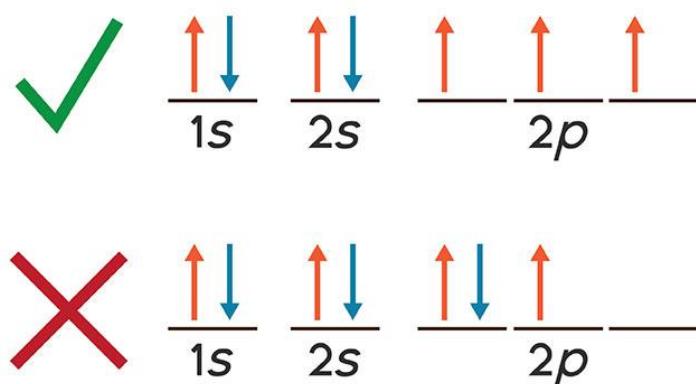


Illustration of Hund's rule in Nitrogen (7 electrons)

- This rule states that when there is orbital degeneracy, the electrons will be arranged to **maximize the total spin**. This means that each electron added to a set of degenerate levels will have the **same parallel spin** as the electron which preceded it. Hund's rule can cause a significant spin imbalance in some materials.
- The physical origin of this rule is Pauli's exclusion principle (two electrons with the same spin can never be found at precisely the same place), and the **repulsive Coulomb interaction energy** (if electrons are far from each other, the overall system energy is lower). The two effects above makes systems with the same spin energetically favorable.
- The difference in energy between the parallel and anti-parallel alignments is the **exchange energy**.

# Magnetic materials

- In case of equal number of electrons with spin up and spin down, the material is **diamagnetic** and the net spin magnetism is zero.
- Many materials behave **paramagnetic**, *i.e.* the electron spins on each atom do not completely cancel; each atom has a net spin and a net magnetic dipole moment ( $\chi_m$  slightly positive).
- Paramagnetic materials remain typically very weakly magnetic because the **individual atomic magnets are uncoupled and point in random directions**. If an external magnetic field is applied, the individual magnets attempt to align with the magnetic field. The energy  $E$  of an atomic dipole of strength  $p_m$  in a field  $H$  is given by:

$$E = -\mu_0 p_m H$$

- At room temperature and usual magnetic fields, the energy of an individual atomic dipole is small compared to  $k_B T$ , and this leads to only a tiny paramagnetic susceptibility.
- The relative permeability  $\mu_r$  of most paramagnetic materials is therefore approximately one, except at very high fields and very low temperatures

# Magnetic materials

- The interesting applications of magnetic materials tend to come not from paramagnetism or diamagnetism, but from arrangements such as **ferromagnetism** where the magnetic moments **remain aligned** even in the absence of an external magnetic field.
- Ferro* is the Latin word for *iron* (this is the reason behind the atomic symbol of iron - Fe), which displays strong magnetic properties.
- In order to understand ferromagnetism we need to consider not just interactions between individual magnetic moments and the external field, but also **interactions between the magnetic moments**.

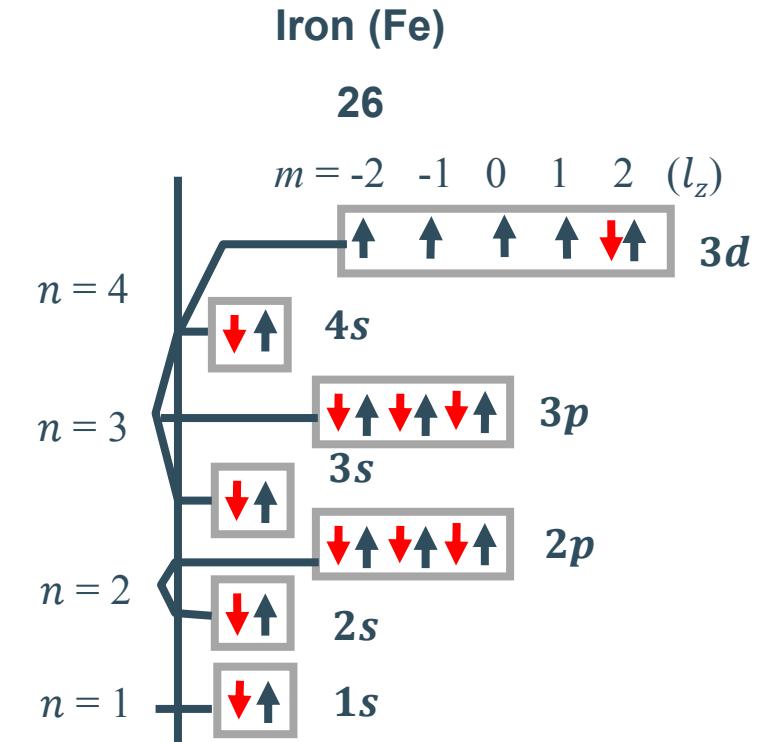


Illustration of Hund's rule for Fe. Notice the spin imbalance in the  $3d$  orbital.

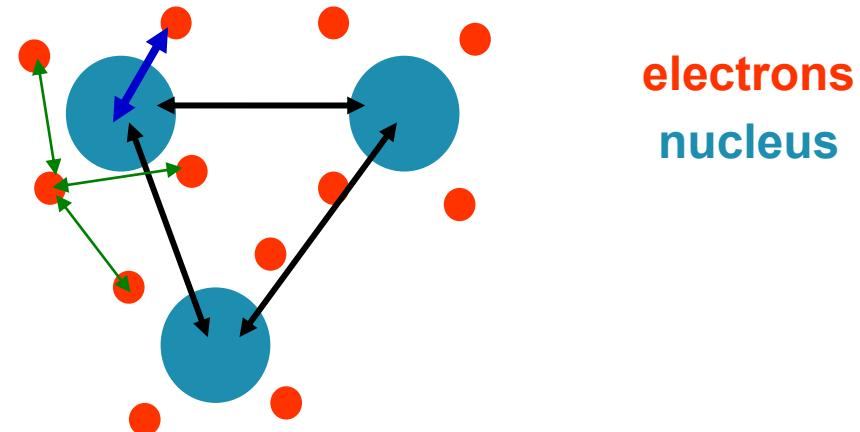
# Magnetic materials

- The periodic arrangement of the spins in these materials results from an electrostatic coupling between the electrons and nucleus of the neighboring atoms, called the **exchange coupling (or energy)**  $U_{ex}$ :

$$U_{ex} = -2J_{ex}\vec{S}_i\vec{S}_j$$

where  $\vec{S}_i$  and  $\vec{S}_j$  are the **spin vectors** on atoms  $i$  and  $j$ , and  $J_{ex}$  is the **exchange integral**, which is related to the overlapping of the electronic orbitals  $i$  and  $j$ .

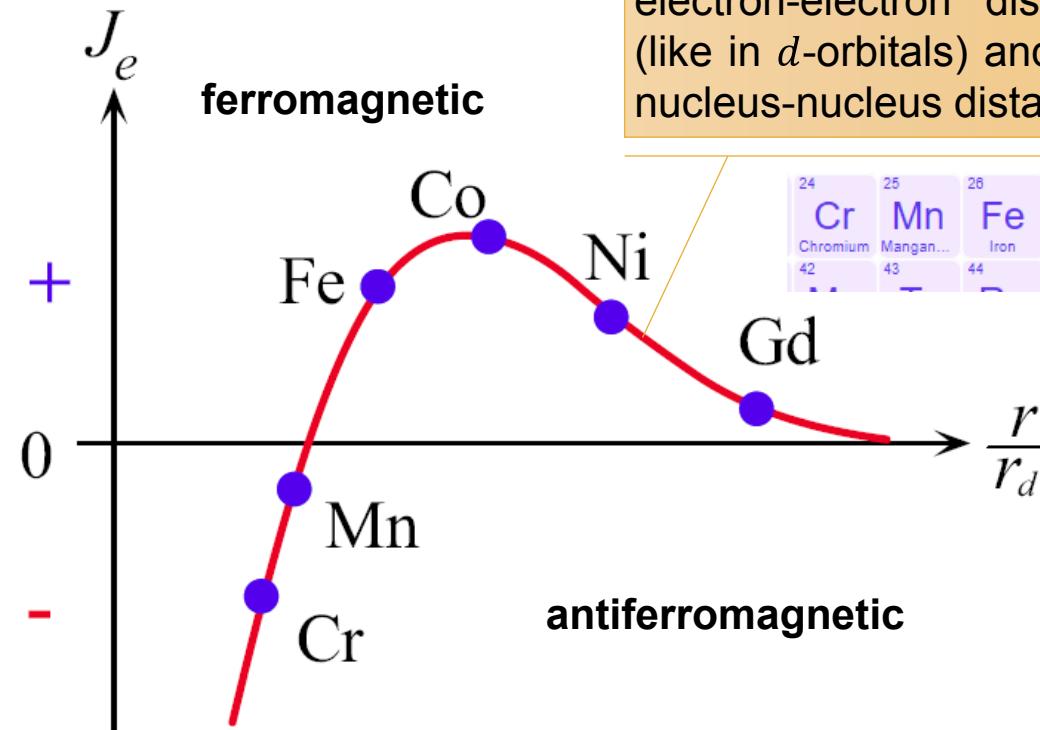
- The exchange integral  $J_{ex}$  is related to the “electron – electron” and “electron – nucleus” interactions of neighboring atoms.



- The exchange interaction is the **source of ferromagnetism**.
- It turns out that  $J_{ex}$  can be *positive* (parallel alignment favored; **ferromagnetism**) or *negative* (anti-parallel alignment favored; **anti-ferromagnetism**).

# Magnetic materials

- If the exchange integral  $J_{ex}$  is **positive**, the exchange coupling is minimal (negative) for parallel spins  $i$  and  $j$ , and the material is **ferromagnetic**
- If the exchange integral  $J_{ex}$  is **negative**, the exchange coupling is minimal for anti-parallel spins  $i$  and  $j$ , and the material is **antiferromagnetic**.



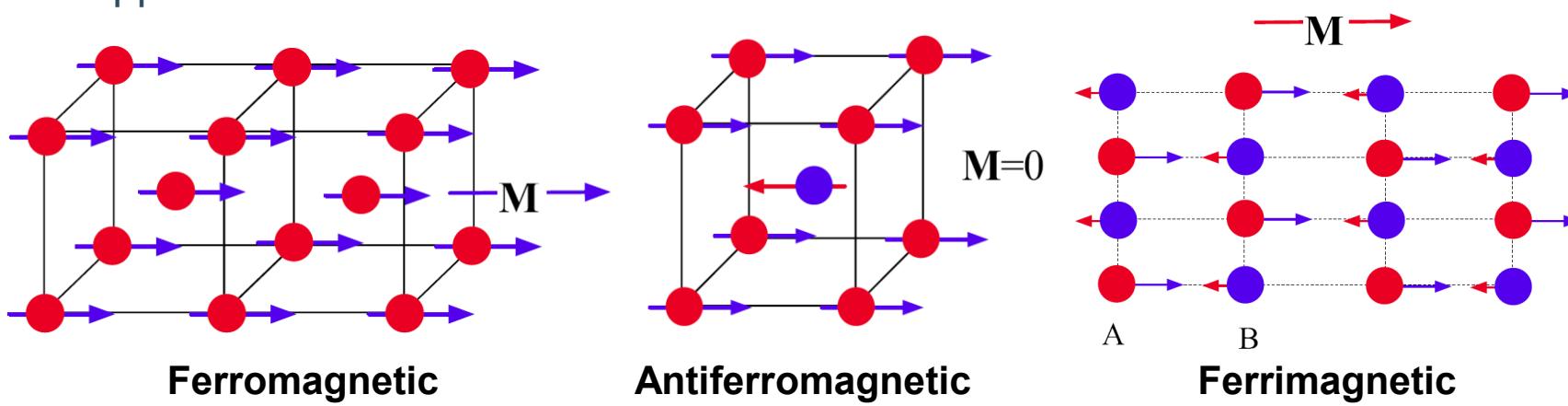
$J_{ex}$  positive for small electron-electron distances (like in  $d$ -orbitals) and large nucleus-nucleus distances.

|          |           |      |        |        |      |
|----------|-----------|------|--------|--------|------|
| 24       | 25        | 26   | 27     | 28     | 29   |
| Cr       | Mn        | Fe   | Co     | Ni     | Cu   |
| Chromium | Mangan... | Iron | Cobalt | Nickel | Copp |

The exchange integral as a function of  $r/r_d$ , where  $r$  is the interatomic distance and  $r_d$  the radius of the  $d$ -orbit (or the average  $d$ -subshell radius). Cr to Ni are transition metals. For Gd, the x-axis is  $r/r_f$  where  $r_f$  is the radius of the  $f$ -orbit.

# Magnetic materials

- In a magnetized region of a **ferromagnetic** material such as iron all the magnetic moments are spontaneously aligned in the same direction. There is a strong magnetization vector  $M$  even in the absence of an applied field.



- In the **antiferromagnetic** BCC crystal (Cr) the magnetic moment of the center atom is cancelled by the magnetic moments of the corner atoms (an eighth of the corner atom belongs to the unit cell).
- In a **ferrimagnetic** crystal. All  $A$ -atoms have their spins aligned in one direction and all  $B$ -atoms have their spins aligned in the opposite direction. As the magnetic moment of an  $A$ -atom is greater than that of a  $B$ -atom, there is net magnetization,  $M$ , in the crystal.

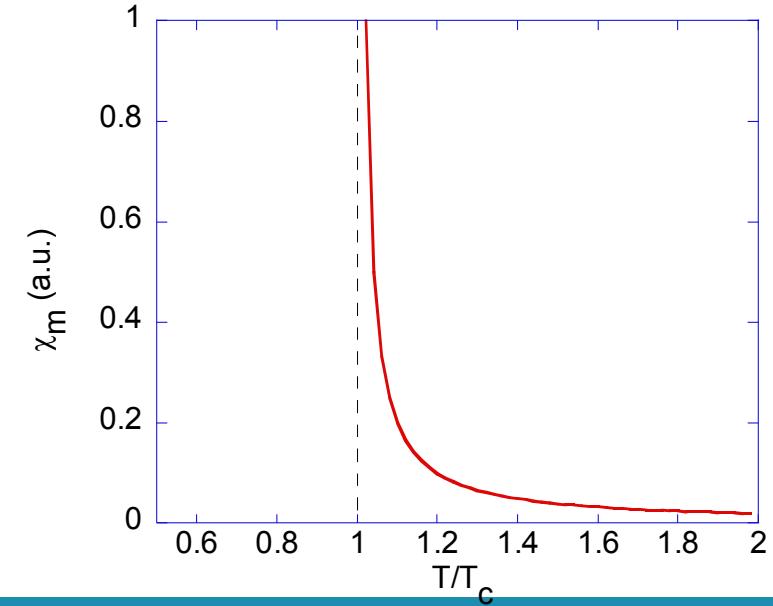
# Ferromagnetic-paramagnetic phase transition

- Ferromagnetic materials exhibit a long-range ordering phenomenon at the atomic level which causes the unpaired electron spins to line up parallel with each other in a region called a **domain**.
- All ferromagnets have a **maximum temperature** where the ferromagnetic property disappears as a result of thermal agitation. This temperature is called the **Curie temperature  $T_c$** . At  $T_c$ , thermal disorder induces a transition from the ordered ferromagnetic phase to a disordered paramagnetic phase.
- The magnetic susceptibility  $\chi_m$  presents a discontinuity at the Curie temperature.

| Material         | Spontaneous magnetization $M$ (G) | $T_c$ (K) |
|------------------|-----------------------------------|-----------|
| Fe               | 1707                              | 1043      |
| Co               | 1400                              | 1388      |
| Ni               | 485                               | 627       |
| CrO <sub>2</sub> | 515                               | 386       |

$$\chi_m = \frac{C}{T - T_c}$$

(with  $C$  the **Curie constant**.)



# Magnetic anisotropy & domains

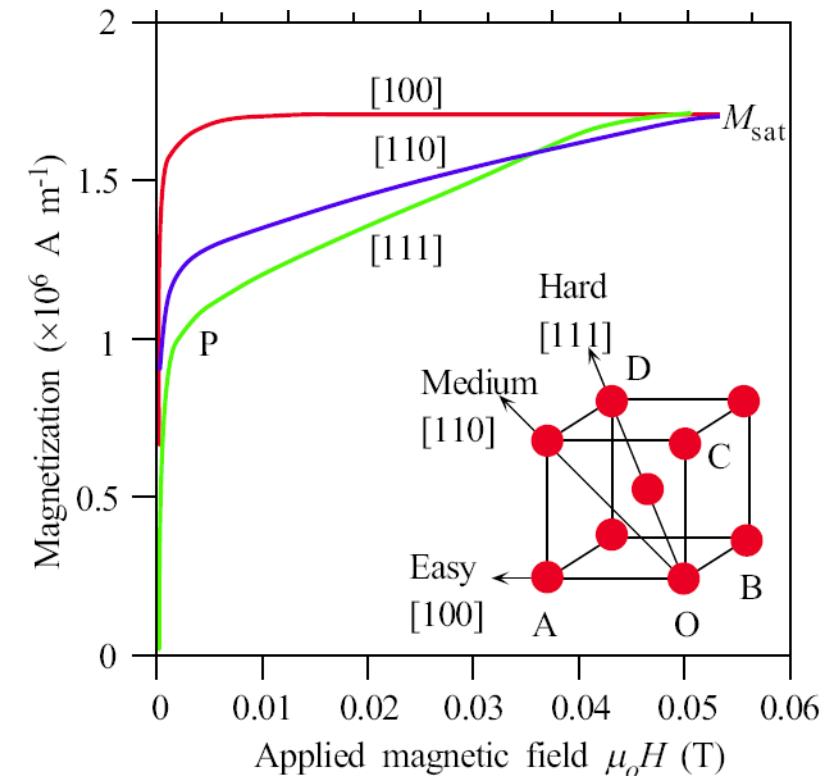


# Magnetic anisotropy

- Most ferromagnetic materials present a **magnetic anisotropy**, i.e. they are preferentially magnetized in a particular direction, called their **easy axis**.
- If  $\varphi$  is the angle between the magnetization  $M$  and the direction of the easy axis, the **anisotropic energy  $U_{an}$**  (energy per volume) is given by:

$$U_{an} = K \sin^2 \varphi$$

with  $K$  the anisotropy constant, which is dependent on material.

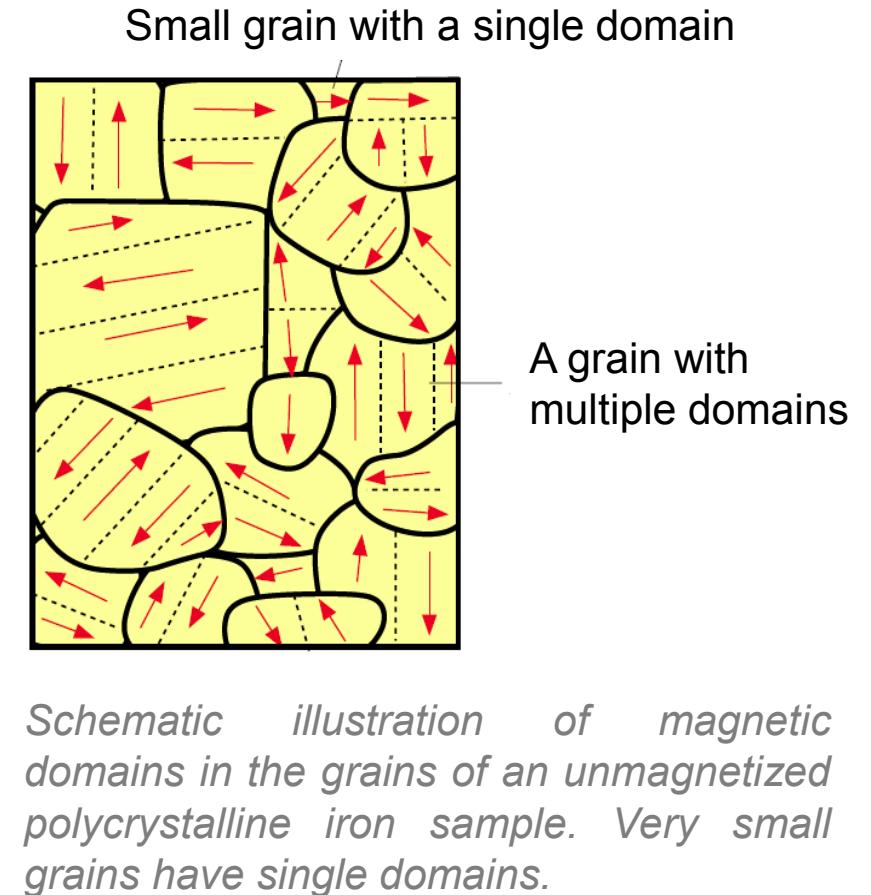


*Magneto-crystalline anisotropy in a single iron crystal.  $M$  versus  $H$  depends on the crystal direction and is easiest along [100] and hardest along [111].*

# Magnetic domains

- At the **atomic scale**, spins of ferromagnetic materials are aligned and parallel. However, at the **macroscopic scale**, not all the spins are necessarily aligned, due to the formation of **magnetic domains**, which all have different orientations for the magnetization  $\vec{M}$ .
- Inside each domain, the magnetization is uniform. However, the relative orientation of  $\vec{M}$  varies from domain to domain.
- When an external magnetic field  $\vec{H}$  is applied to the material, all the domains **tend to orient  $\vec{M}$  parallel to  $\vec{H}$** , to reduce the energy (per volume) of the system:

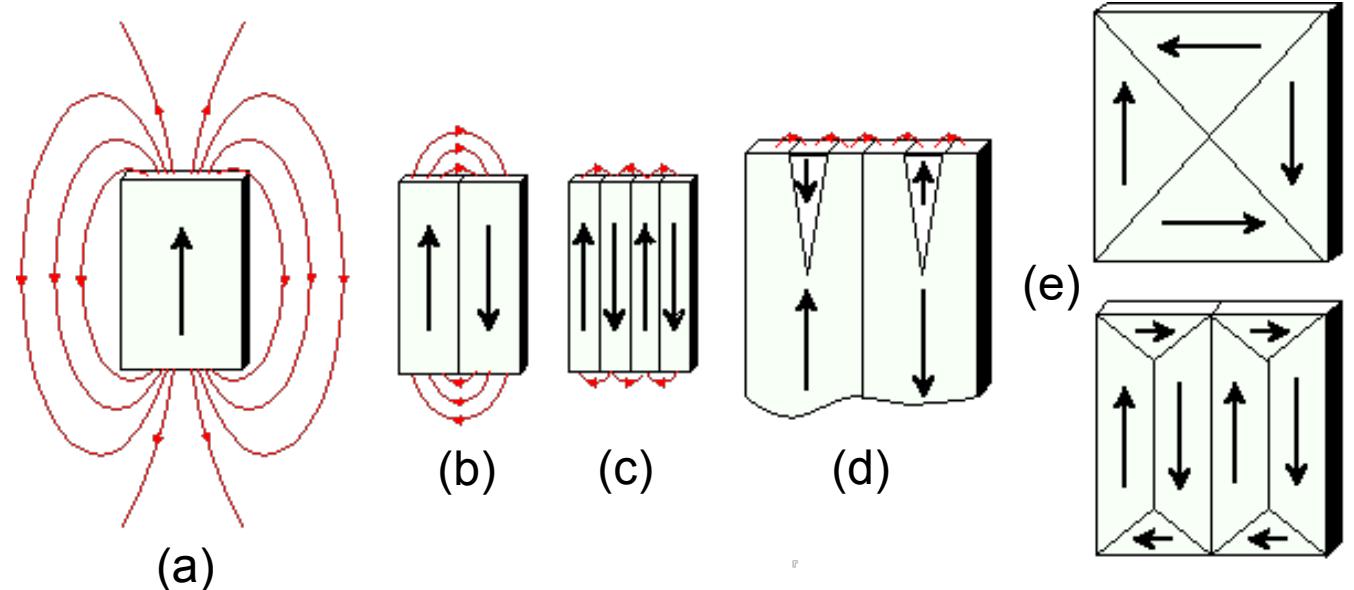
$$E_H = -\mu_0 \vec{M} \cdot \vec{H} = -\mu_0 M H \cos(\theta) [\text{J/m}^3]$$



# Magnetic domains

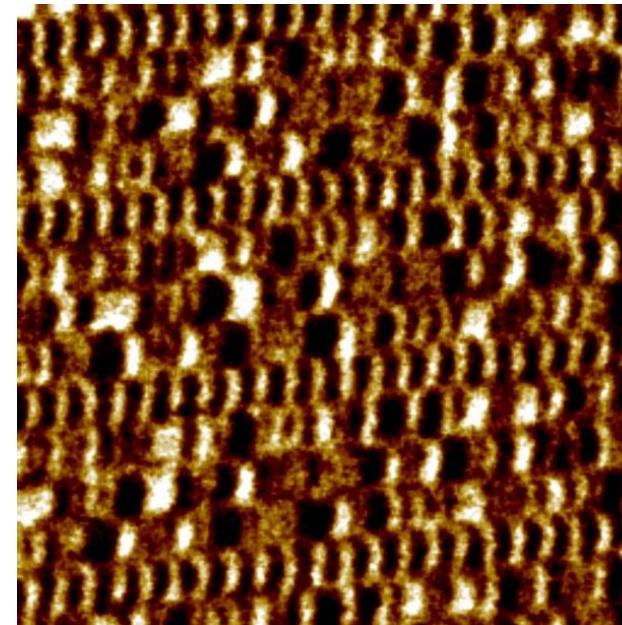
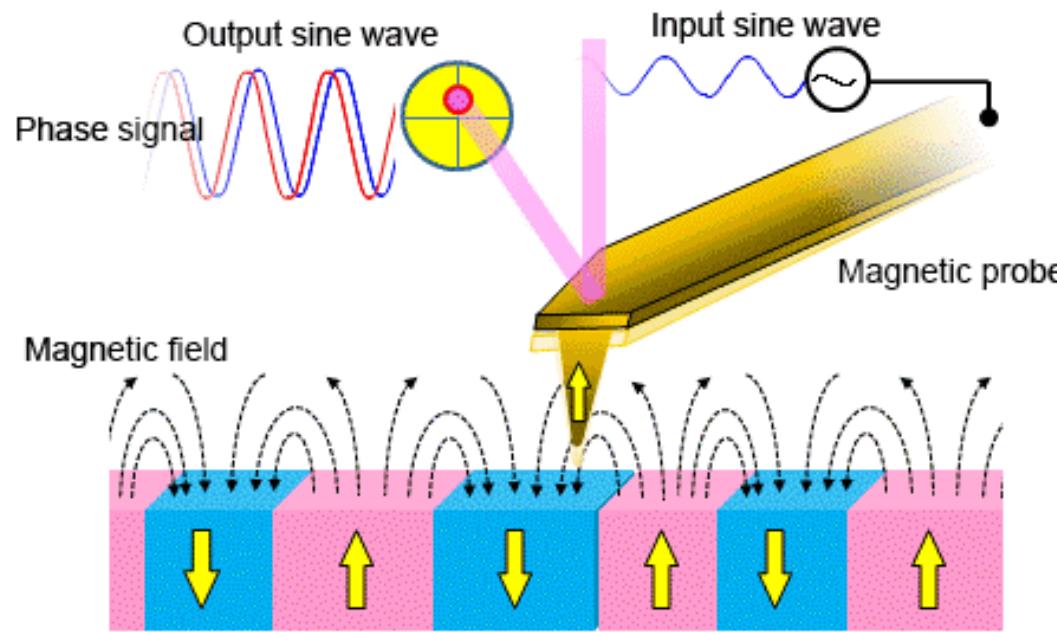
- The formation of domains does have some **energetic cost**. The exchange interaction in a ferromagnet aligns spins because that reduces the total energy of the system. At a **domain wall** (the boundary between two domains), where the perfect ferromagnetic alignment gets disrupted, the local energy should in principle be higher.
- However, the increase in exchange energy is balanced by a **net savings in stray field energy**.

*Illustration of stray magnetic field from a sample with a uniaxial anisotropy with (a) single magnetized domain, (b) two and (c) four domains. (d) Reverse spike domains which can form in a uniaxial domain structure. (e) Flux closure domains which prevent any stray flux from emerging from the sample.*

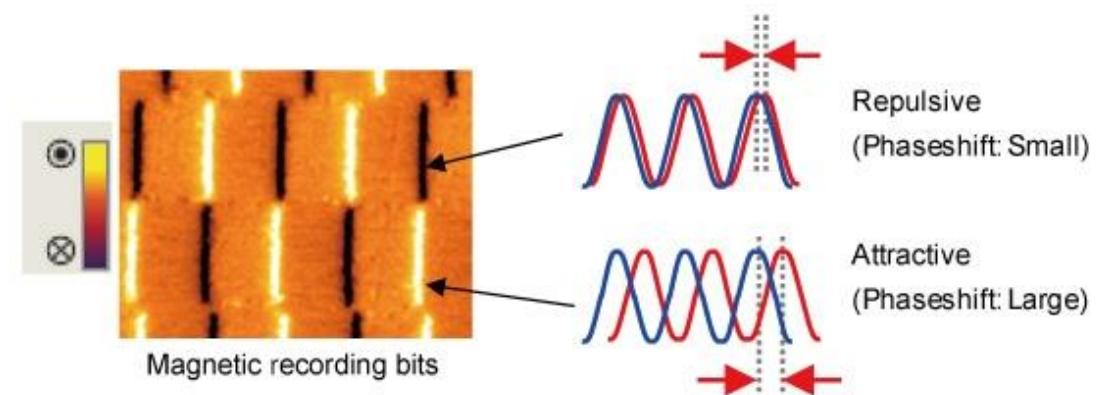


# Magnetic domains

- Magnetic domains can be measured by MFM (magnetic force microscopy).



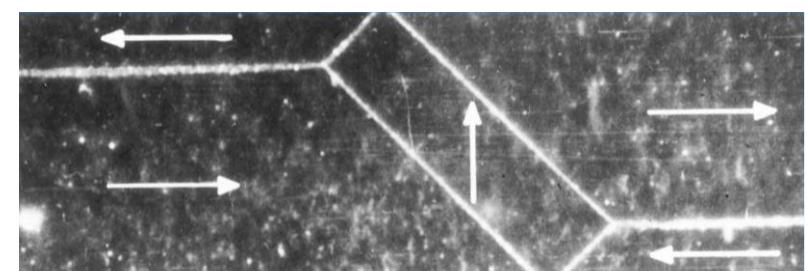
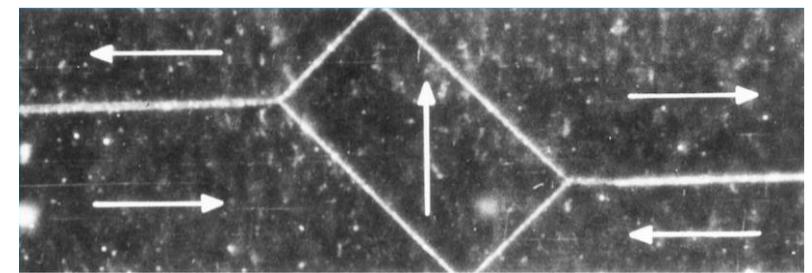
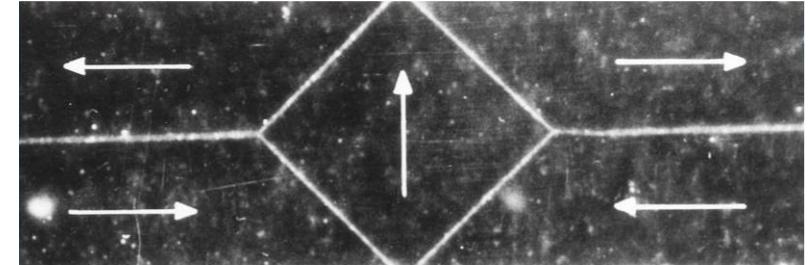
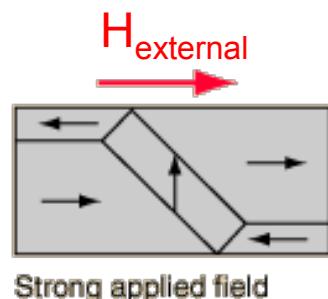
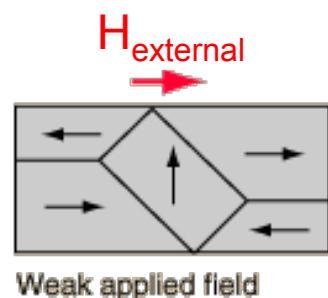
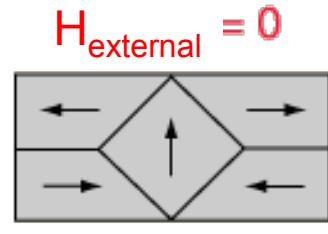
<http://www.parkafm.co.kr/index.php/kr/medias/resources/afm-images>



<https://www.hitachi-hightech.com/global/products/science/tech/em/spm/descriptions/electro/mfm.html>

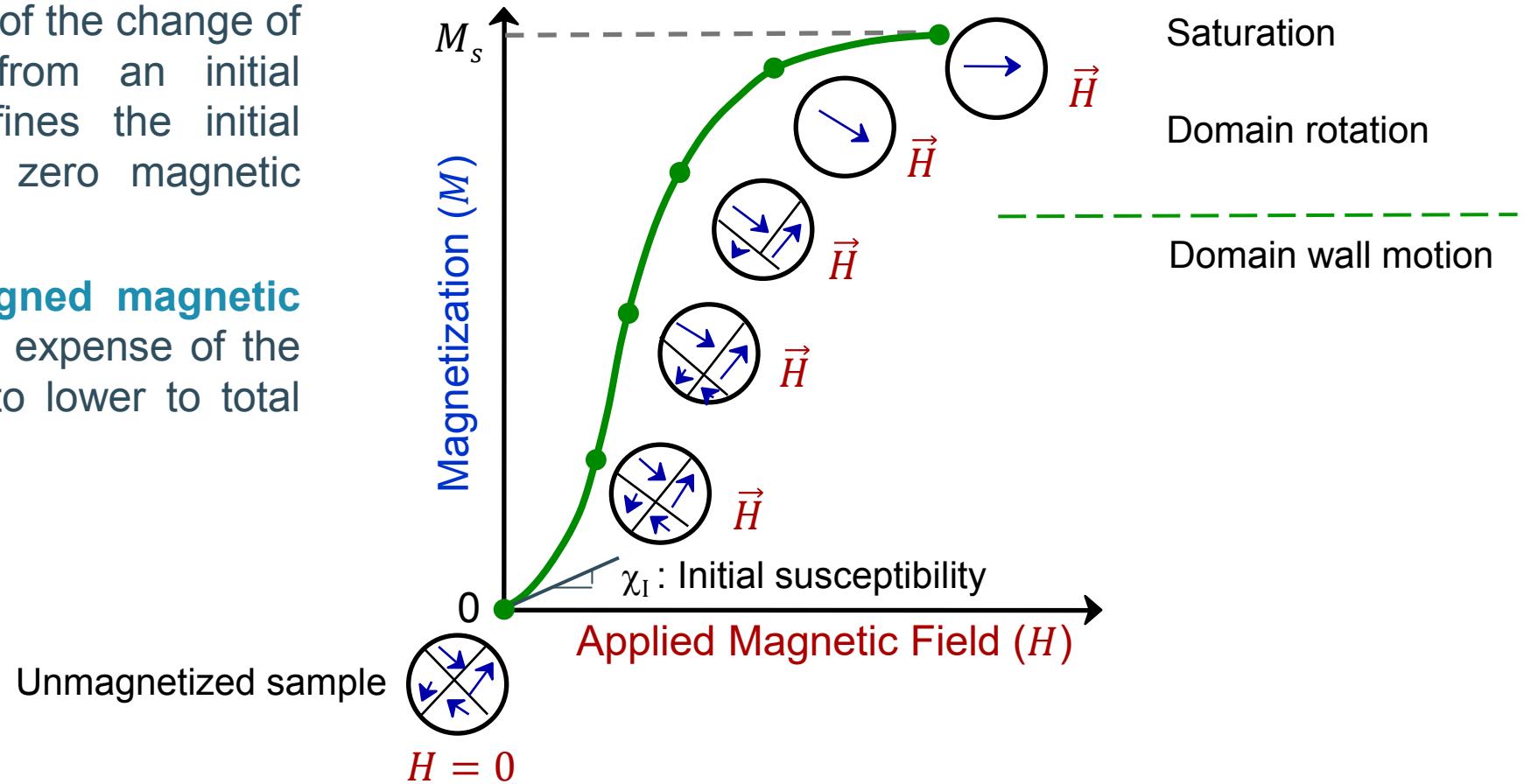
# Magnetic domains

- These pictures illustrate the change of magnetic domains from unmagnetized (at zero field) state to magnetized (under field) state.



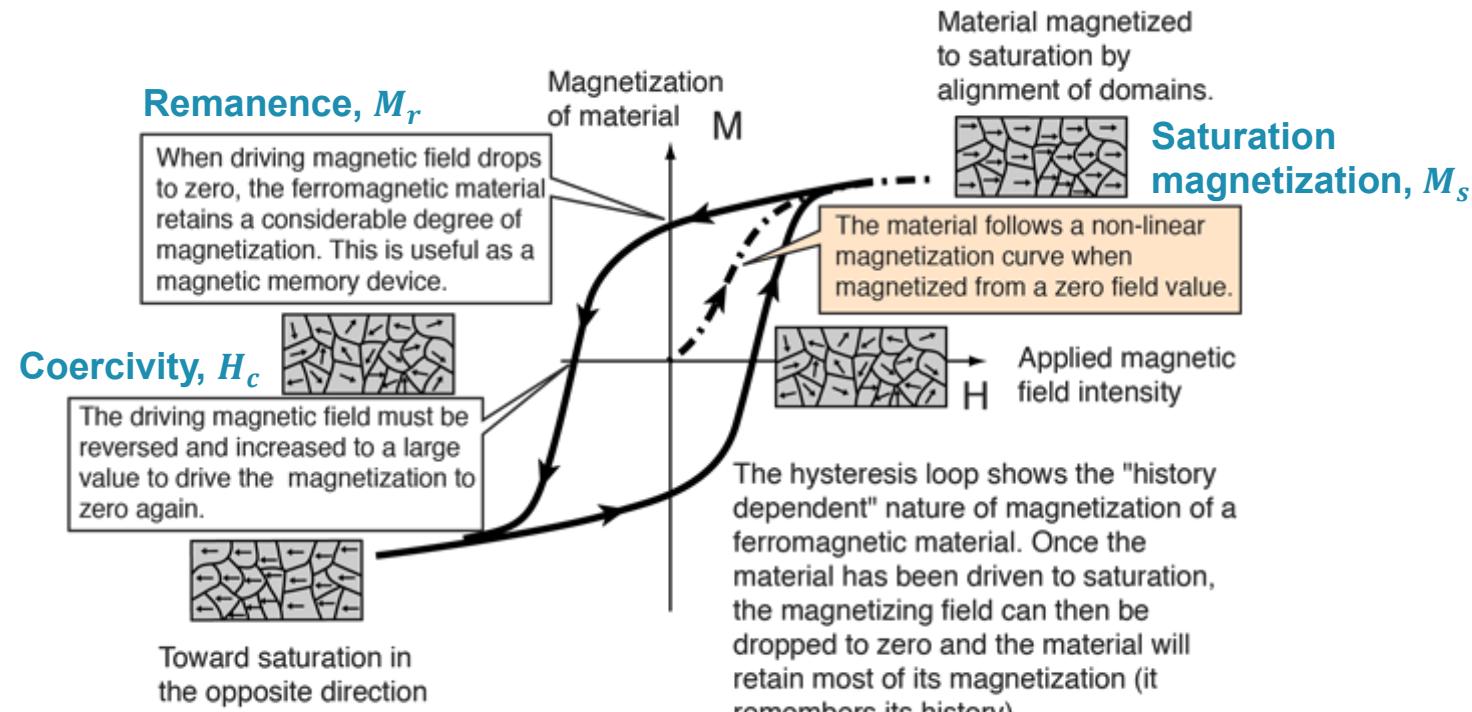
# Magnetic domains

- Schematic illustration of the change of magnetic domains from an initial condition (which defines the initial susceptibility  $\chi_I$ ) at zero magnetic field to **saturation**.
- Domains with an **aligned magnetic moment grow** at the expense of the poorly aligned ones to lower total energy.



# Magnetic hysteresis

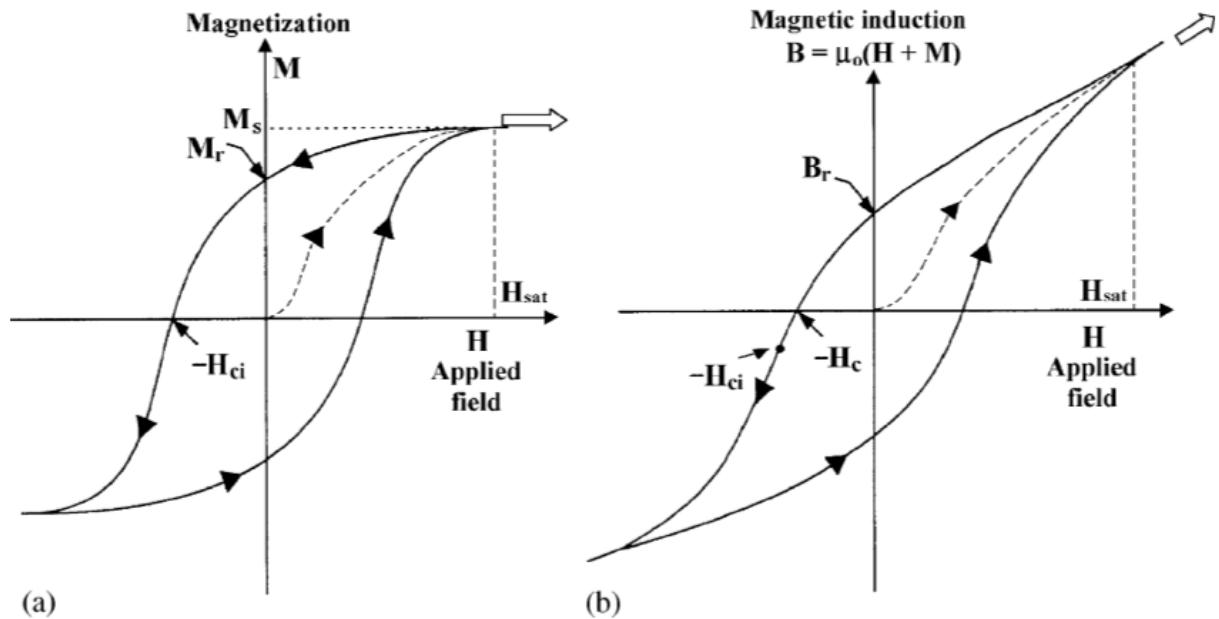
- When a ferromagnetic material is magnetized in one direction, it will not relax back to zero magnetization when the imposed magnetizing field is removed.
- It must be driven back to zero by a field in the opposite direction. If an alternating magnetic field is applied to the material, its magnetization will trace out a loop called a **hysteresis loop**. This is related to the existence of magnetic domains in the material.
- Once the magnetic domains are reoriented, it takes some energy to turn them back again.



<http://hyperphysics.phy-astr.gsu.edu/hbase/Solids/hyst.html>

# Magnetic hysteresis

- It is customary to plot the magnetization  $M$  as a function of the magnetic field strength  $H$ , since  $H$  is a measure of the externally applied field which drives the magnetization.
- There is a distinction between the two notions of '**coercivity**' referred to the  $B(H)$  curve and the  $M(H)$  curve, which turns out to be often confused in textbooks and scientific literature



*Hysteresis curves for a ferromagnetic material: (a)  $M$  vs.  $H$ :  $M_r$  is the remnant magnetization at  $H = 0$ ;  $H_{ci}$  is the intrinsic coercivity, i.e. the reverse field that reduces  $M$  to zero;  $M_s$  is the saturation magnetization; (b)  $B$  vs.  $H$ :  $B_r$  is the remanent induction (or 'remanence') at  $H = 0$ ;  $H_c$  is the coercivity, i.e. the reverse field required to reduce  $B$  to zero.*

H.W.F. Sung and C. Rudowicz, *Magnetism and Magnetic Materials* 260, 250–260 (2003)

# Short note on S.I. versus c.g.s. units

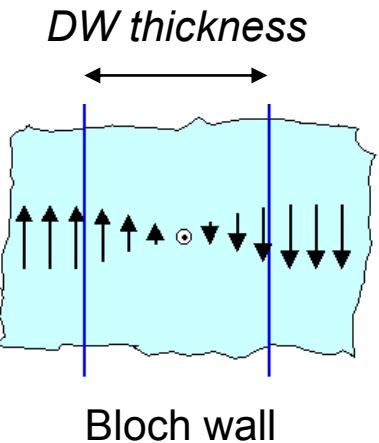
Many people think there is one system called “*The Metric System*”, but actually there are two systems:

- One is the “Système International” or S.I. system, which is the “real” (upper-case) Metric System, which uses Metres, Kilograms and Seconds for length, mass and time. For this reason it is sometimes called the **MKS system**.
- The “other” (lower-case) metric system uses centimeters, grams and seconds. It is most often called the **c.g.s. system**, and sometimes it is called the Gaussian system or the electrostatic system. There are other traditional differences in the two systems when measuring charge and electric and magnetic fields, for example.
- The S.I. unit for magnetic field is the **Tesla, or T**. It comes from the cross-product equation for magnetic force on a moving particle:  $F = qv \times B$ . The magnetic field,  $B$ , must be in units of force per charge per velocity. So  $1 T = 1 \text{ Ns/(Cm)}$ .
- In c.g.s. units, the equation for magnetic force looks different. Instead of  $qv \times B$ , it is  $(qv/c) \times B$ . You have to divide by the speed of light,  $c$ . The unit for magnetic field,  $B$ , is called the **Gauss, G**, where  $1 G = 1 \text{ dyne/esu}$  (esu = statcoulomb) The Earth’s magnetic field at the surface is about  $1/2 G$ , which makes it a very popular unit.
- Tesla’s are bigger than Gauss:  **$1 T = 10^4 G$** .

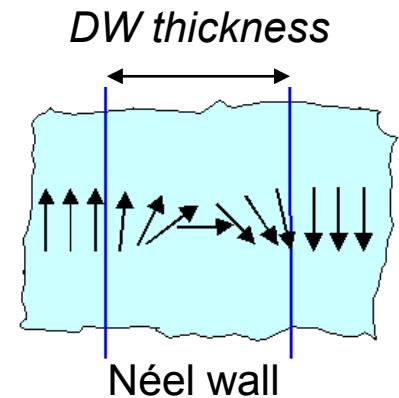
<https://www.physics.utoronto.ca/~jharlow/teaching/Units.htm>

# Domain walls

- Because of the strength of the exchange interaction, which wants to align neighboring spins, **abrupt changes in magnetization direction** (on the atomic scale) costs a lot of **extra energy**. As a result, the local magnetization spreads the change in direction out **over some distance**, i.e. the domain wall **thickness**.
- There are different kinds of domain walls that are possible:

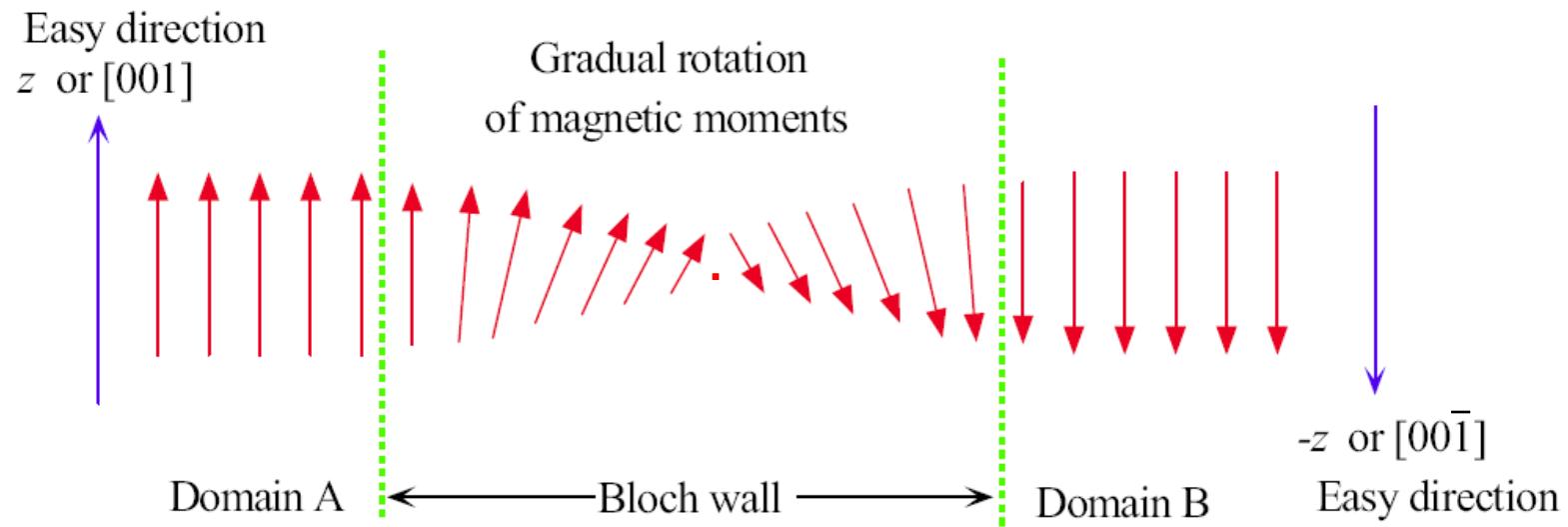


- In a **Bloch wall** the magnetization reverses direction by rotating out of plane, over some number of lattice sites. Energetically favored in thick materials.
- In a **Néel wall** the magnetization rotates in its plane to reverse direction. Favored in thin materials.



# Ferromagnetic domains

- Let's take a closer look into the formation of a **Bloch wall** with a  $180^\circ$  change in the easy axis between two domains.



*In a Bloch wall the neighboring spin magnetic moments rotate gradually, and it takes several hundred atomic spacings to rotate the magnetic moment by  $180^\circ$ .*

- The spins in the material will **gradually rotate** to the opposite magnetization direction. The domain wall will **adjust** its thickness to **minimize the total energy**.
- This total energy is the **sum of the exchange energy** and the **anisotropy energy**.

# Ferromagnetic domains

- The exchange coupling tends to minimize the angle between two adjacent spins, in order to minimize the **exchange energy**:

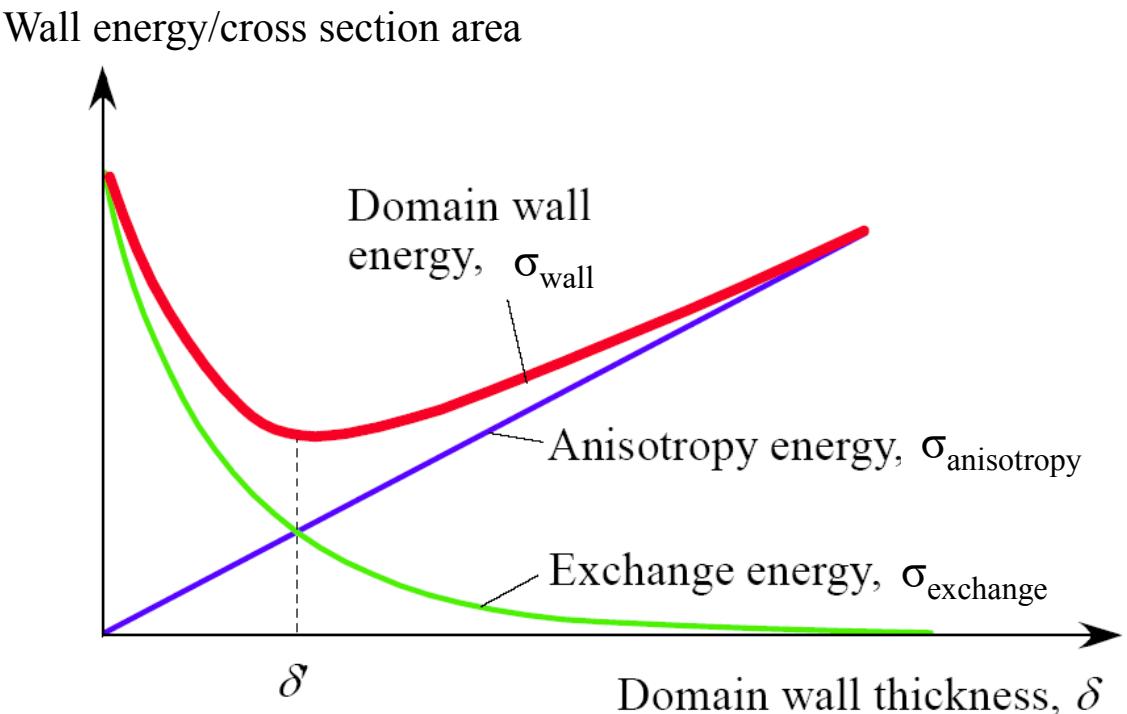
$$U_{ex} = -2J_{ex}\vec{S}_i\vec{S}_j = -2J_{ex}S_iS_j \cos\varphi$$

As a result, the extension of the region between 2 domains (i.e. the domain wall width) would tend to be very large due to this contribution.

- The **anisotropy energy** (per volume) tends to reduce the angle between the magnetization and the easy axis:

$$U_{an} = K \sin^2 \varphi$$

In the transition region, the spins are usually not parallel to the easy axis, such that this contribution tends to minimize the domain wall width.



*Schematic illustration of the potential energy per surface area generated by the anisotropy energy and the exchange energy as a function of the thickness of the domain wall.*

# Ferromagnetic domains

- Consider a change of spin orientation by an angle of  $180^\circ$  between two domains.
- For an infinitesimal change in angle between two adjacent spins, the exchange energy between the two spins reads:

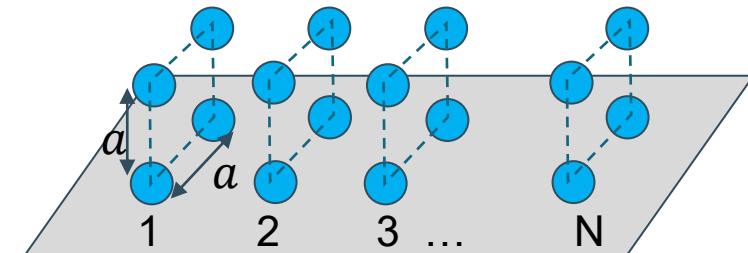
$$\Delta U_{ex} \approx J_{ex} S^2 \varphi^2 \text{ (see details in next slide)}$$

If the total change in angle ( $180^\circ$ ) takes place over  $N$  atoms, then the smallest change is  $\varphi = \pi/N$ . The total exchange energy over these  $N$  atoms then reads:

$$N\Delta U_{ex} \approx J_{ex} S^2 \frac{\pi^2}{N} \text{ (see details in next slide)}$$

- If the lattice constant of the material is  $a$ , then the energy per cross-sectional surface area of the domain wall, due to the exchange coupling is:

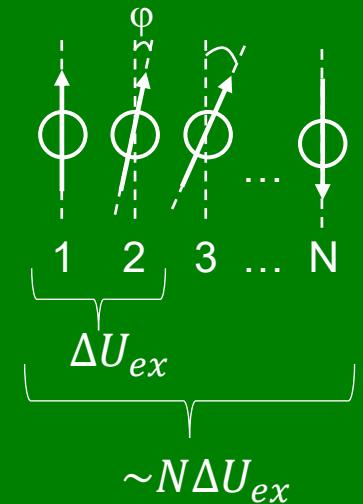
$$\sigma_{ex} \approx J_{ex} S^2 \frac{\pi^2}{Na^2}$$



## Ferromagnetic domains (extra)

- $U_{ex} = -2J_{ex}\vec{S}_i\vec{S}_j = -2J_{ex}S_iS_j \cos\varphi$   $\begin{cases} \text{if } \vec{S}_i \parallel \vec{S}_j \rightarrow U_{ex,0} = -2J_{ex}S^2 \overset{1}{\underset{1-\frac{\varphi^2}{2}}{\cos 0}} \Rightarrow \vec{S}_i \uparrow \uparrow \vec{S}_j \\ \text{if } \vec{S}_i \nparallel \vec{S}_j \rightarrow U_{ex,1} = -2J_{ex}S^2 \overset{\cos\varphi}{\underset{1-\frac{\varphi^2}{2}}{\cos\varphi}} \Rightarrow \vec{S}_i \uparrow \nearrow \vec{S}_j \end{cases}$   $\varphi$  is very small:  $\lim_{\varphi \rightarrow 0} \cos\varphi \approx 1 - \frac{\varphi^2}{2}$  (Taylor series)
- $\Delta U_{ex} = U_{ex,1} - U_{ex,0} = -2J_{ex}S^2 \left(1 - \frac{\varphi^2}{2} - 1\right) = J_{ex}S^2\varphi^2$
- The total spin flip ( $\varphi_{\text{total}} = \pi$ ) occurs over  $N$  atoms. Then  $\varphi = \pi/N$  and  $\Delta U_{ex} = J_{ex}S^2 \frac{\pi^2}{N^2}$
- The total energy to flip the spin is then:

$$N\Delta U_{ex} = J_{ex}S^2 \frac{\pi^2}{N}$$



# Ferromagnetic domains

- Over the domain wall, the maximum variation of the anisotropy surface energy (the energy per cross-sectional surface area of the domain wall) equals:

$$\sigma_{an} \approx KNa$$

where  $Na$  is the width of the domain (remember that  $U_{an}$  was energy per volume).

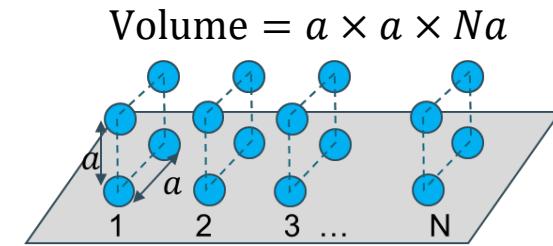
- The total surface energy is then:

$$\sigma \approx J_{ex}S^2 \frac{\pi^2}{Na^2} + KNa$$

- This energy is minimal when:

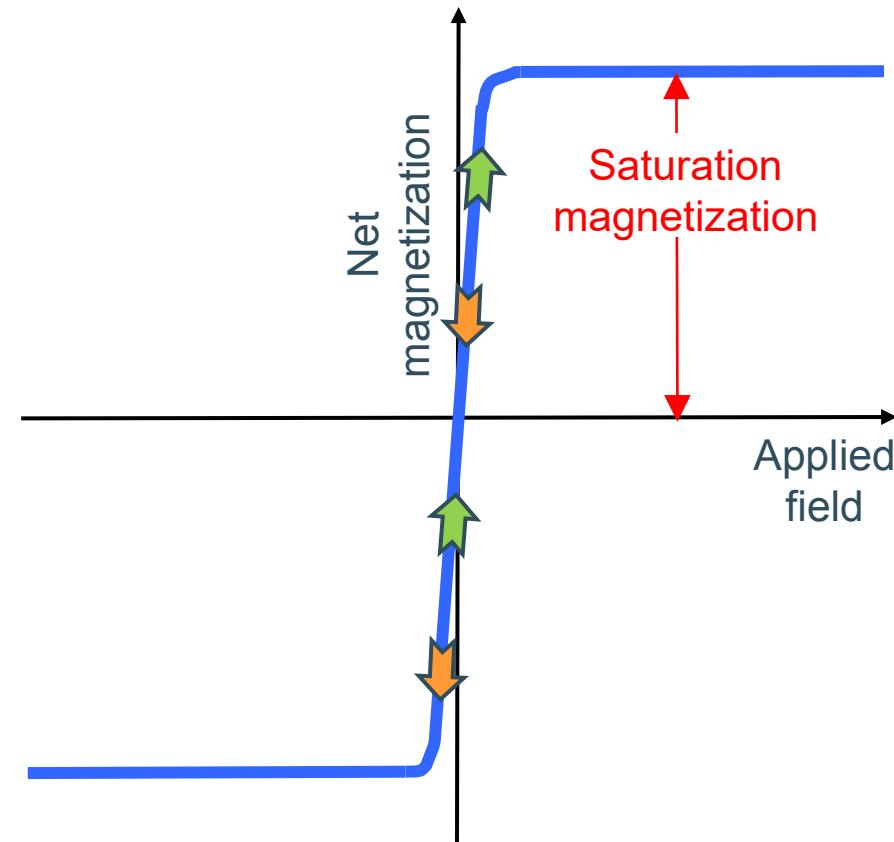
$$\frac{\partial\sigma}{\partial N} = 0 \Rightarrow \frac{-\pi^2 J_{ex} S^2}{N^2 a^2} + Ka = 0 \Rightarrow \delta = Na = \sqrt{\frac{\pi^2 J_{ex} S^2}{Ka}}, \text{ with } \delta \text{ the domain wall width.}$$

- This means that the domain wall width depends strongly on the **anisotropy constant  $K$**  of the material (it can change over few orders of magnitude). Materials with a **large** anisotropy constant  $K$  material typically have domain walls in the order of  $\sim 10$  nm. Materials with a **small**  $K$  value have much wider domain walls that can range from  $\sim 1$  to  $10$   $\mu\text{m}$ .



# Soft and hard magnets

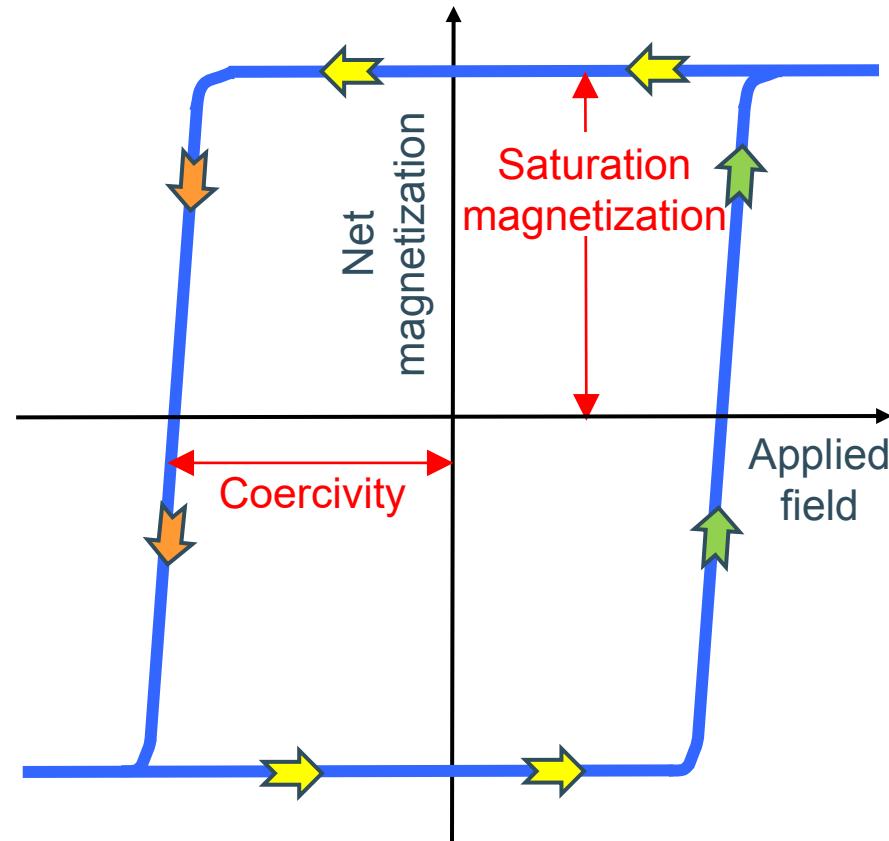
- Two type of ferromagnetic materials are distinguished, based on their response relative to an external magnetic field:



- In **soft magnetic materials**, the magnetization of the different domains can be easily switched by the applied magnetic field. This leads to the **absence of hysteresis** on the magnetization vs magnetic field curve.
- These materials can **change** their state of magnetization many times each second, and are used for AC applications (transformers, recording heads).

# Soft and hard magnets

- Two type of ferromagnetic materials are distinguished, based on their response relative to an external magnetic field:



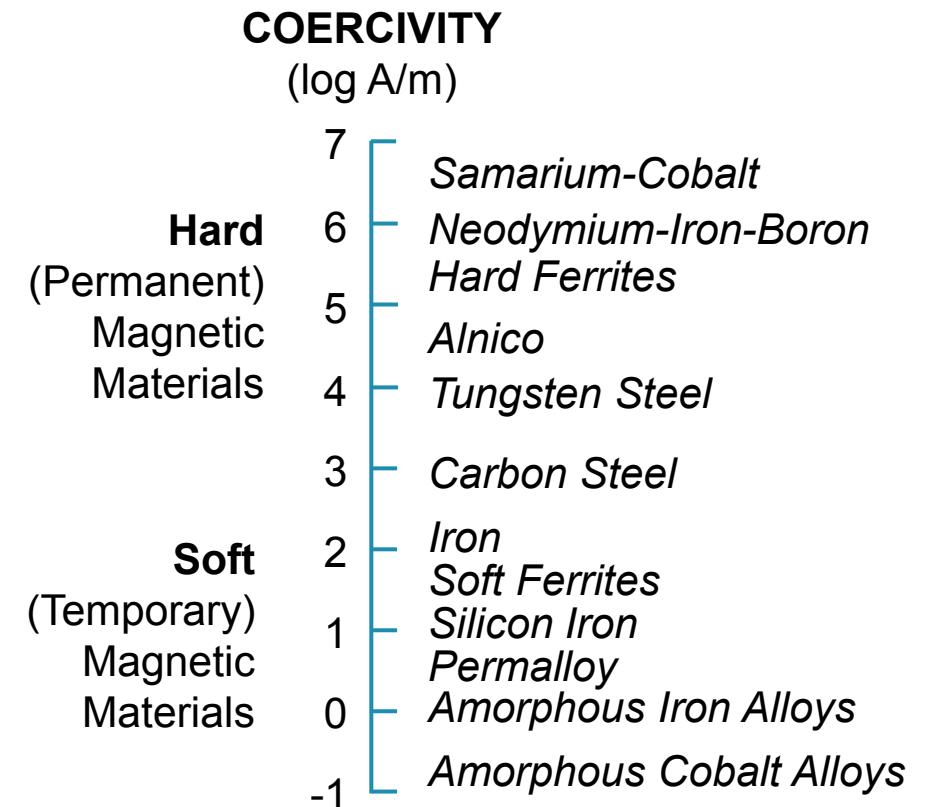
- In **hard magnetic materials**, the magnetization of the different domains cannot be switched easily, leading to a **hysteresis** on the field curve that shows the magnetization versus the magnetic field.
- These materials **maintain** their magnetization state over time and are used as permanent magnet and magnetic memory devices.

# Soft and hard magnets

- A magnetic material is **soft or hard**, depending whether **domain-wall motion** (switching of magnetization between different domains) is **easy or difficult**. This depends much on the microstructure of the material.
- Inhomogeneous materials, with many grain boundaries (poly-crystalline phases), present local variation of the surface energy  $\gamma$  of domain walls, which makes domain wall motion more difficult. Defects can act as ‘pinning’ sites and **impede the domain wall motion**, especially if the domain walls are narrow, i.e. if  $K$  is high.
- Therefore, hard magnets are typically inhomogeneous high- $K$  materials (the anisotropy constant).

# Soft and hard magnets

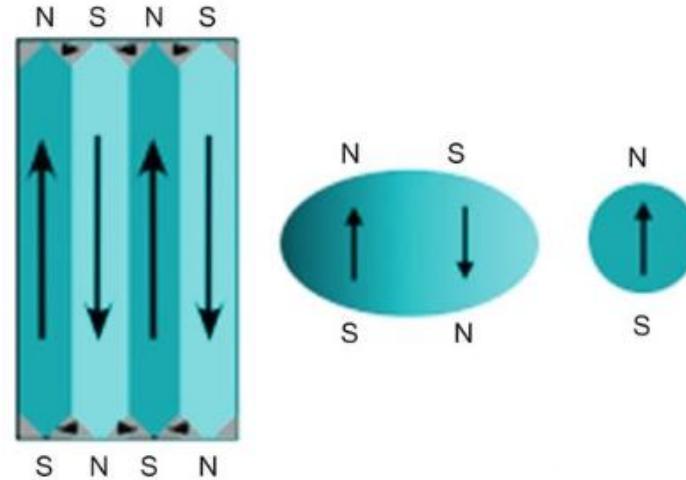
- Homogeneous **low- $K$  materials**, with only few **grain boundaries** and structural defects, have large domain walls with lower surface energy, leading to much **easier motion** of spins at the boundaries between different domains
- Soft magnets are usually homogeneous low- $K$  materials.
- Magnetic materials with a broad range of coercivities are available.
- The **coercivity** is an extrinsic property and, therefore, is sensitive to the micro-structure of the material.



*Range of coercivities (note log scale) available for various magnetic materials.*

# Magnetic domains: size effect

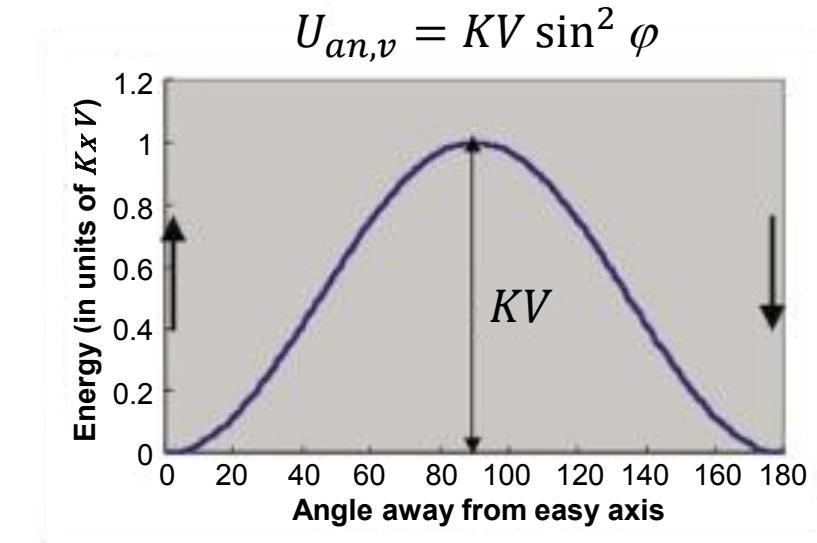
- The average **size** of the magnetic domains is a function of the system energy.
- As the volume of a piece of magnetic material is reduced the number of domains decreases.



- It is clear that when the volume drops below a certain critical value, it becomes energetically unfavorable to include a domain wall and the **uniformly magnetized state** becomes the **lowest energy** configuration. Thus, a piece of magnetic material below the **critical size** stays permanently magnetized at close to its saturation magnetization.

# Magnetic domains: size effect

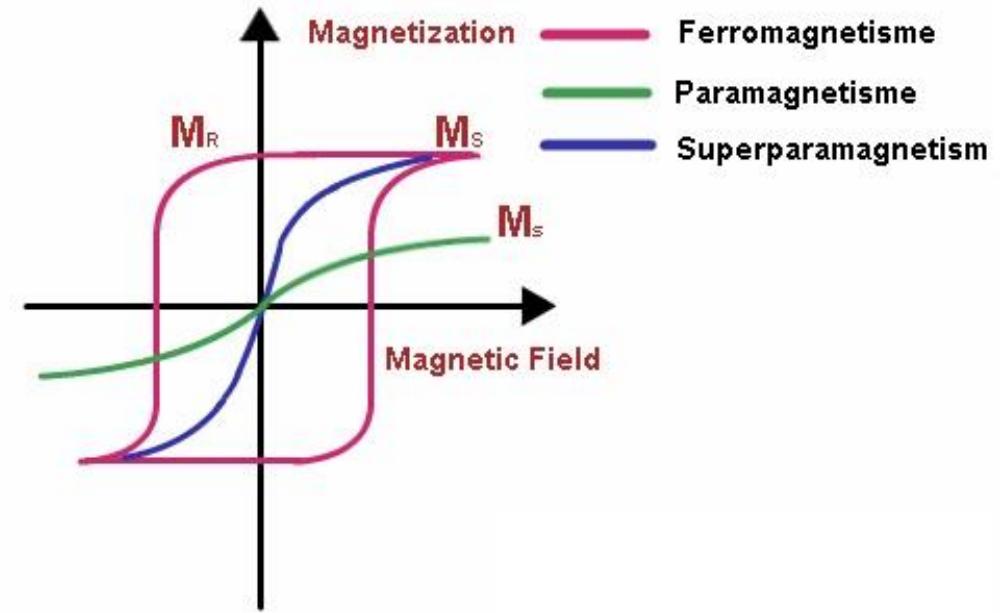
- Consider a particle with a uniaxial anisotropy whose anisotropy energy is given by  $U_{an,v} = KV \sin^2 \varphi$ , where  $K$  is the anisotropy energy density (in  $\text{J.m}^{-3}$ ),  $V$  is the particle volume and  $\varphi$  is the angle between the magnetization vector and the easy axis.
- The system therefore has **two minimal energy** states separated by an **energy barrier** of height  $KV$ .
- As the volume decreases at a specific temperature, there comes another critical diameter at which the magnetization of the nanoparticle is unstable against **thermal fluctuations**, that is,  $KV \sim k_B T$  and the time averaged magnetization goes to zero.
- Thus for a given particle size, there is a temperature that marks the transition from a permanent static moment to one that is fluctuating in a nanoparticle.



*Dependence of anisotropy energy on magnetization direction in a nanoparticle with a uniaxial anisotropy.*

# Superparamagnetism

- This means that in sufficiently small nanoparticles, magnetization can **randomly flip direction**, especially at high temperature. The nanoparticles are said to be in the **superparamagnetic state**.
- Normally, any ferromagnetic or ferri-magnetic material undergoes a transition to a paramagnetic state above its Curie temperature. Superparamagnetism is different from this transition since it occurs **below the Curie temperature** of the material and the magnetization is high.
- In the "macro-spin approximation" it is assumed that under this condition the magnetization of the nanoparticles can be considered as a single **giant magnetic moment**, which is the sum of all the individual magnetic moments carried by the atoms of the nanoparticle.



*Under the influence of a magnetic field paramagnetic materials are slightly magnetized, but when the magnetic field is removed this magnetization goes to zero. On the contrary, ferromagnetic materials present a strong saturation magnetization and a remanent magnetization ( $M_R$ ) in the absence of the magnetic field. Superparamagnetic materials share properties of ferromagnetism and paramagnetism.*

# Superparamagnetism

- Due to the magnetic anisotropy of the nanoparticle, the magnetic moment has usually only **two stable orientations** antiparallel to each other, separated by an **energy barrier**  $KV$ . At finite temperature, there is a finite probability for the magnetization to flip and reverse its direction. The mean time between two flips is called the **Néel relaxation time**  $\tau_N$  and is given by the Néel-Arrhenius equation:

$$\tau_N = \tau_0 \exp\left(\frac{KV}{k_B T}\right)$$

with  $\tau_N$  the average time it takes for the nanoparticle's magnetization to randomly flip as a result of thermal fluctuations,  $\tau_0$  the attempt period (characteristic of the material),  $K$  is the nanoparticle's magnetic anisotropy energy density and  $V$  its volume.  $KV$  is therefore the energy barrier associated with the magnetization moving from its initial easy axis direction, through a "hard plane", to the other easy axis direction.  $k_B$  is the Boltzmann constant and  $T$  the temperature.

- The Néel relaxation time is an exponential function of the **grain volume**, which explains why the flipping probability becomes rapidly **negligible for bulk materials or large nanoparticles**.

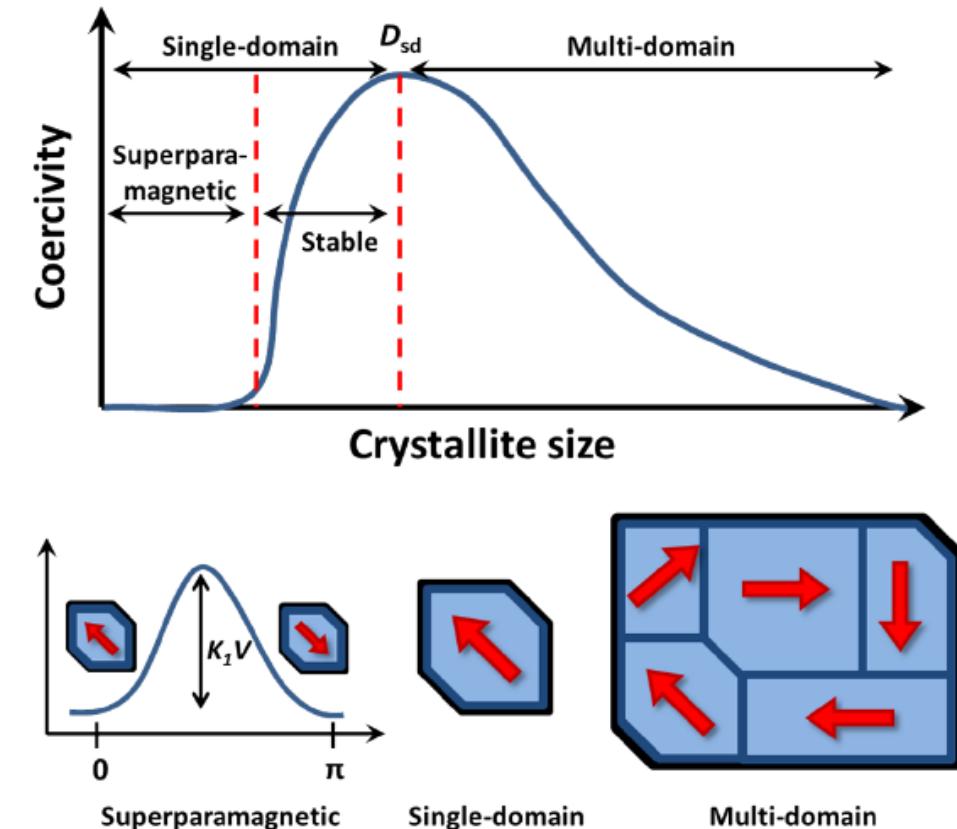
# Superparamagnetism

- Let us imagine that the magnetization of a single magnetic nanoparticle is measured and let us define  $\tau_m$  as the measurement time.
  - If  $\tau_m \gg \tau_N$ , the **nanoparticle magnetization** will flip several times during the measurement and the measured magnetization will **average to zero**.
  - If  $\tau_m \ll \tau_N$ , the magnetization will not flip during the measurement and the measured magnetization will be what the instantaneous magnetization was at the beginning of the measurement.
- In the former case, the nanoparticle will appear to be in the **superparamagnetic** state whereas in the latter case it will appear to be “blocked” in its initial state.
- The state of the nanoparticle (superparamagnetic or blocked) depends on the measurement time. A transition occurs when  $\tau_m = \tau_N$ . Typical in experiments, the measurement time is kept constant and the temperature is varied. Under these conditions the transition between the superparamagnetic and the blocked state is observed at a specific temperature for which  $\tau_m = \tau_N(T)$  is satisfied. This temperature is called the **blocking temperature**, given by:

$$T_B = \frac{KV}{k_B \ln \left( \frac{\tau_m}{\tau_0} \right)}$$

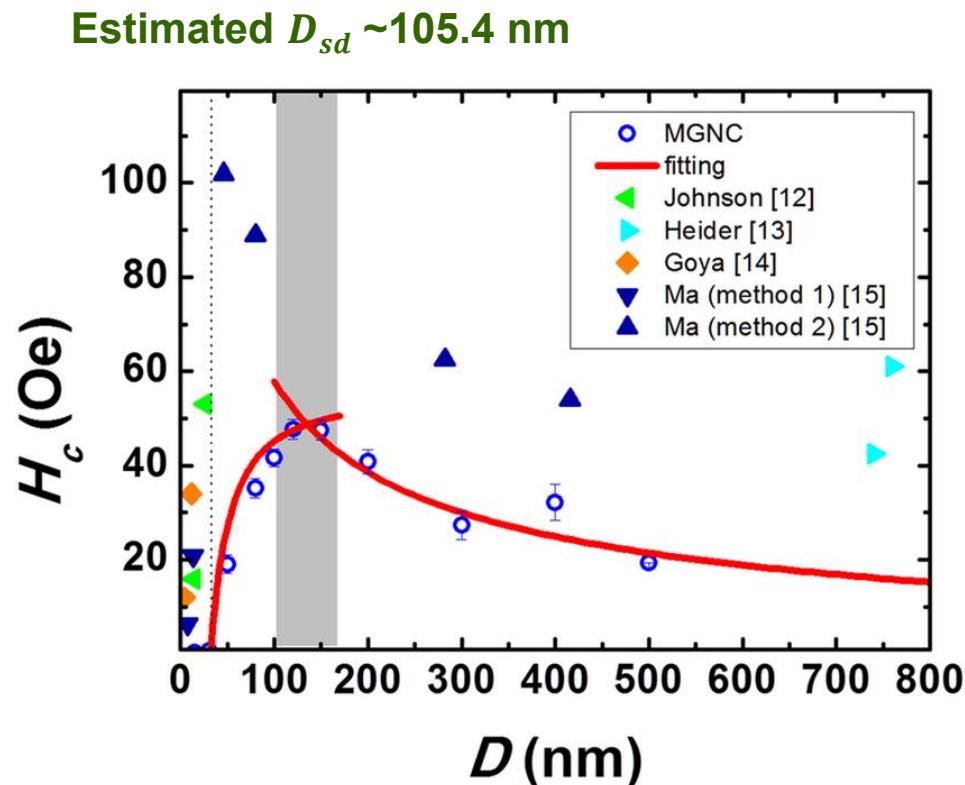
# Size effect on coercivity

- Unlike saturation magnetization, which is, in principle, size-independent, the coercivity is very sensitive to the **size variation**. With decreasing particle size the coercivity of a particle gradually increases to a **maximum value** at a particular size and then rapidly decreases to zero as the particle size further decreases
- Larger crystallites divide into magnetic domains separated by domains walls, which lowers the coercivity of the materials. The highest coercivity is achieved at the **critical magnetic single-domain size** ( $D_{sd}$ ). The decrease of coercivity below  $D_{sd}$  is due to an increased thermal contribution, which randomizes the magnetization. When the particle size decreases further, the coercivity becomes zero, reaching a superparamagnetic state. Unlike the transition from ferromagnetic to ordinary paramagnetic properties in bulk magnets, the ferromagnetic-to-superparamagnetic **transition** in fine particles is solely due to the size effect.

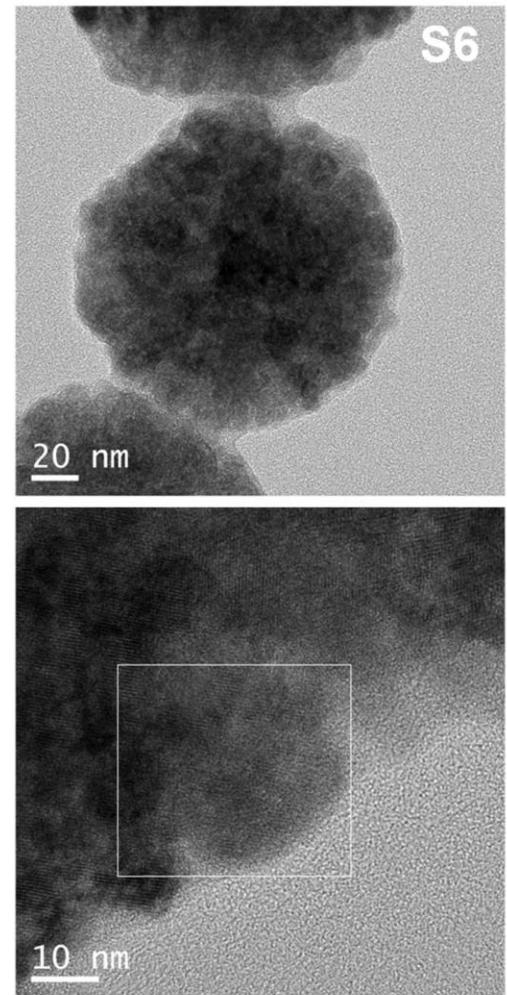
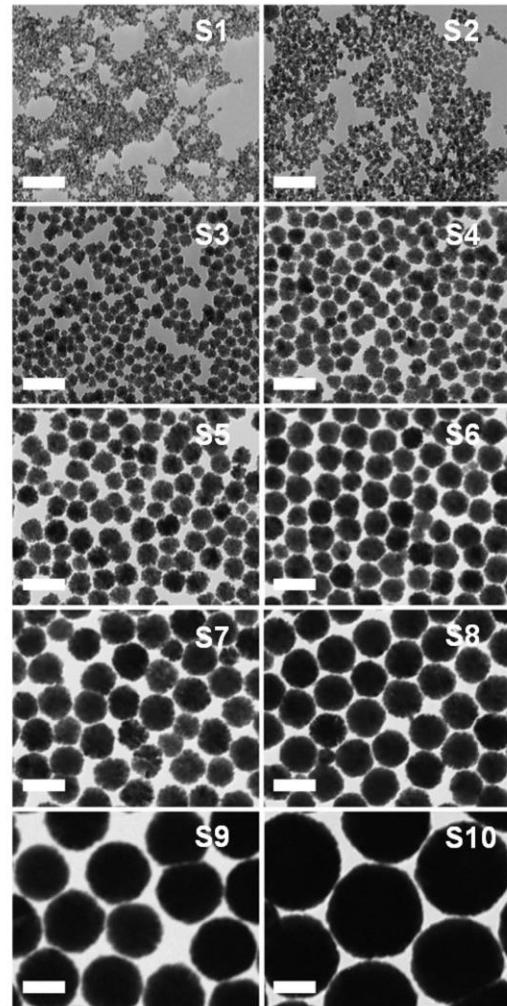


# Size effect on coercivity

- The size effect on coercivity was experimentally verified on the polyol synthesis of magnetite ( $\text{Fe}_3\text{O}_4$ ) nano-particles by adjusting the chemistry.



Scale bars are 200 nm.



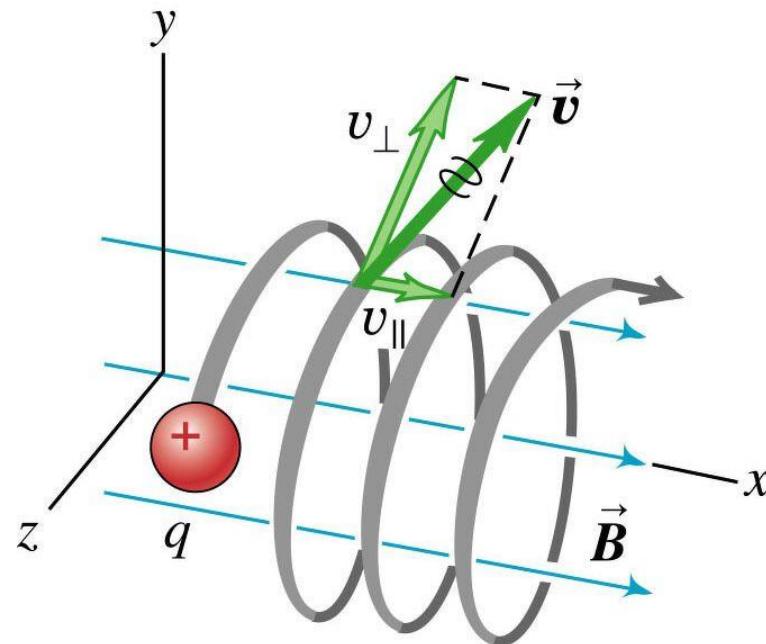
J. S. Lee et al., Sci. Rep. 5, 12135 (2015)

# Spin transport



# Magnetism and electrical resistivity

- The **magnetoresistance** phenomena is the tendency of a material to change the value of its electrical resistance in an externally-applied magnetic field.



## Ordinary Magneto Resistance (OMR)

- The Lorentz force  $\vec{F}$  due to magnetic field modifies the trajectory of electrons :

$$\vec{F} = -q\vec{v} \times \vec{B}$$

- The Ordinary Magneto Resistance (Lord Kelvin, 1856) results in small changes of the bulk resistivity, typically only  $\Delta R / R < 5\%$ .

- The scalar resistivity is given by:

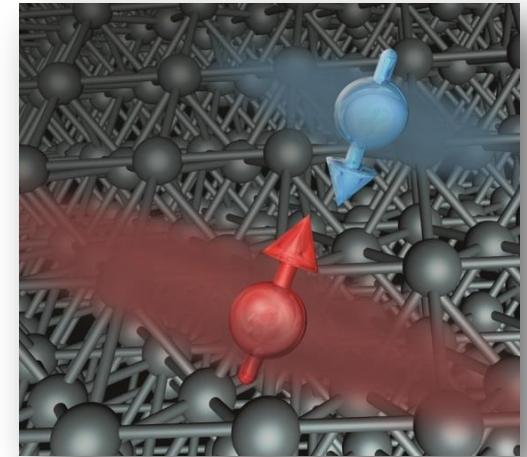
$$\rho_{xx} = \frac{1 + (\mu B)^2}{\sigma_0}$$

where  $B$  is the magnetic field and  $\mu$  the electron mobility.

- Since this effect is rather small, it is not very useful for practical applications.

# Spin polarized transport

Much more interesting applications can be obtained by using **spin-polarized currents**. Spin-polarized transport will occur naturally in any material for which there is an **imbalance of the spin populations** at the Fermi level. This imbalance commonly occurs in **ferromagnetic metals**.

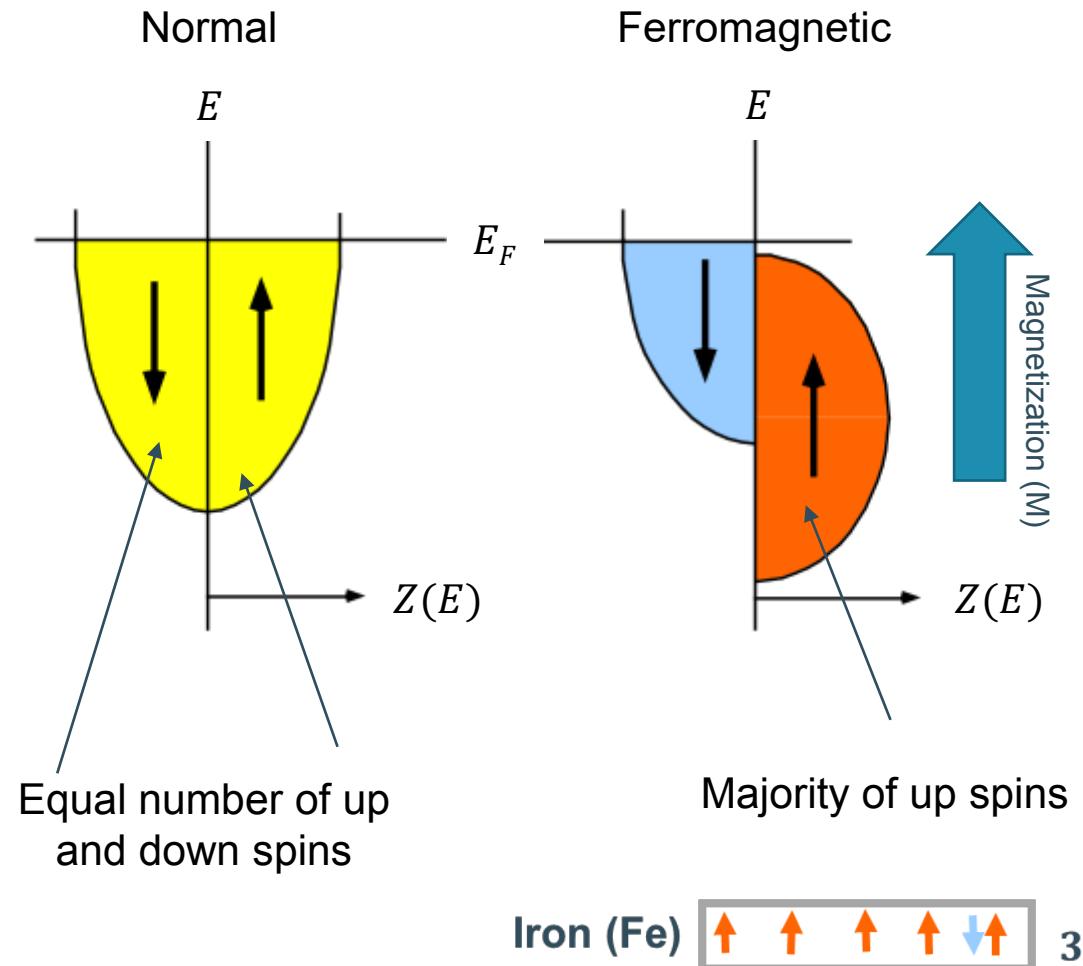


## Mott model

- In the Mott model it is proposed that the electrical conductivity in metals can be described in terms of two largely **independent conducting channels**, corresponding to the **up-spin** and **down-spin** electrons, and electrical conduction occurs in parallel for the two channels.
- In non-magnetic conductors the scattering rate does not depend on the electron spin. However, in ferromagnetic metals the **scattering rates** of the up-spin and down-spin electrons **are different**. Mostly it is assumed that the **scattering is strong for electrons with spin anti-parallel** to the magnetization direction and **weak for electrons with spin parallel** to the magnetization direction (in a bulk material).

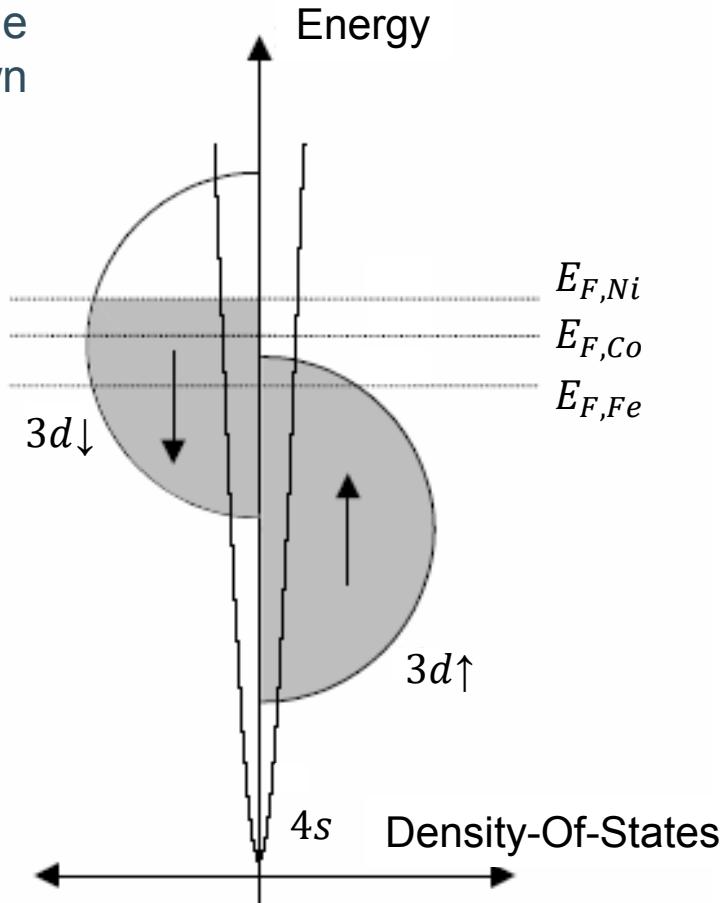
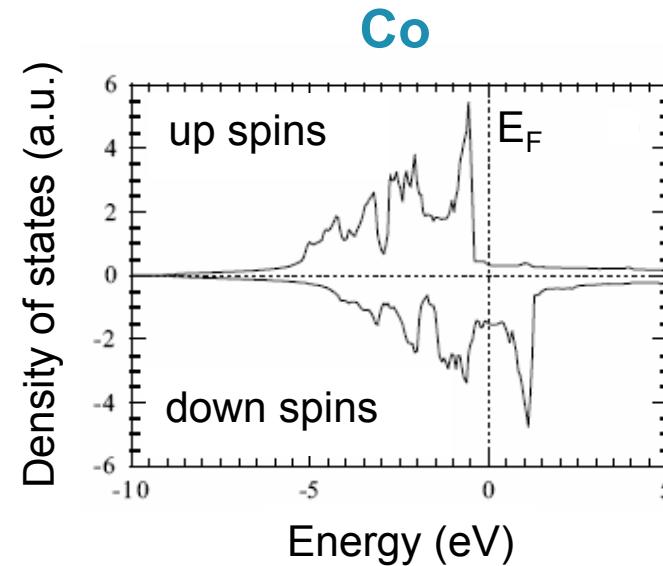
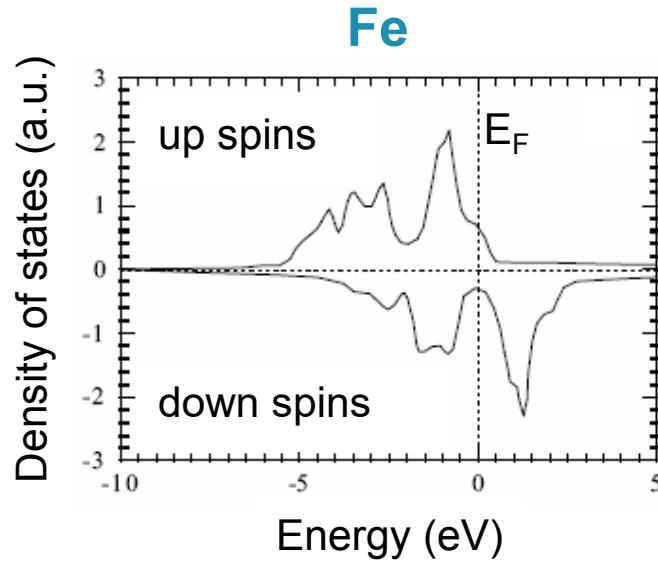
# Band structure of magnetic materials

- The density of states  $Z(E)$  as a function of energy  $E$  is then usually presented as in the right figure.
  - Non-magnetic materials show an **equal number** of up and down spins in the DOS.
  - Ferromagnetic materials have a **majority** of electrons in one spin state (up-state by convention).
- In this schematic diagram, it is seen that for the ferromagnetic material the available majority spin states (up-state) are **completely filled** at the Fermi level, while this is **not the case** for the **minority** spin states (down-state).
- This is a direct consequence of the **spin imbalance** present in these materials due to **Hund's rule**.



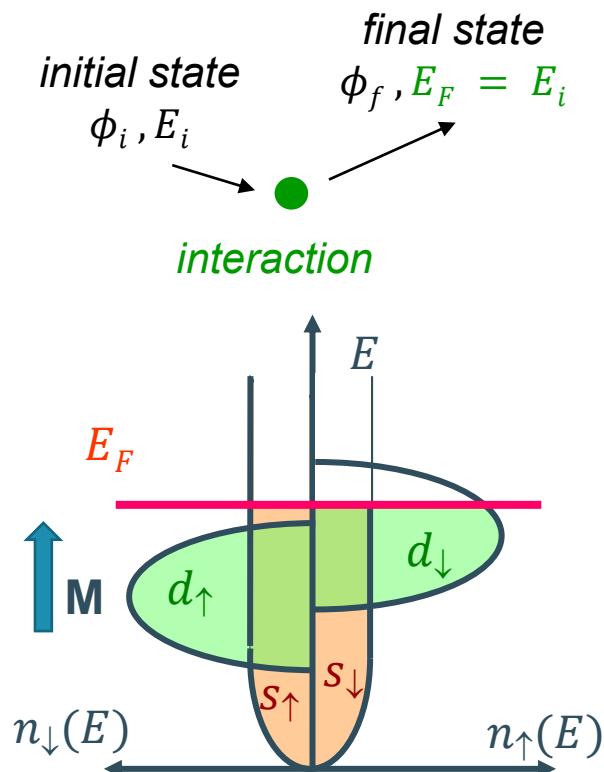
# Band structure of magnetic materials

- In general, in ferromagnetic materials there is an **asymmetry** present near the Fermi level where the Density-Of-States (DOS) of the “d” orbital is larger for down spins with respect to up spins. (The “s” orbital is symmetric).
- For Ni, Co and Fe these differences in the **3d orbitals** can be easily observed.
- There is a different band structures for up spin and down spin electrons .



# Spin dependent transport in the diffusion limit

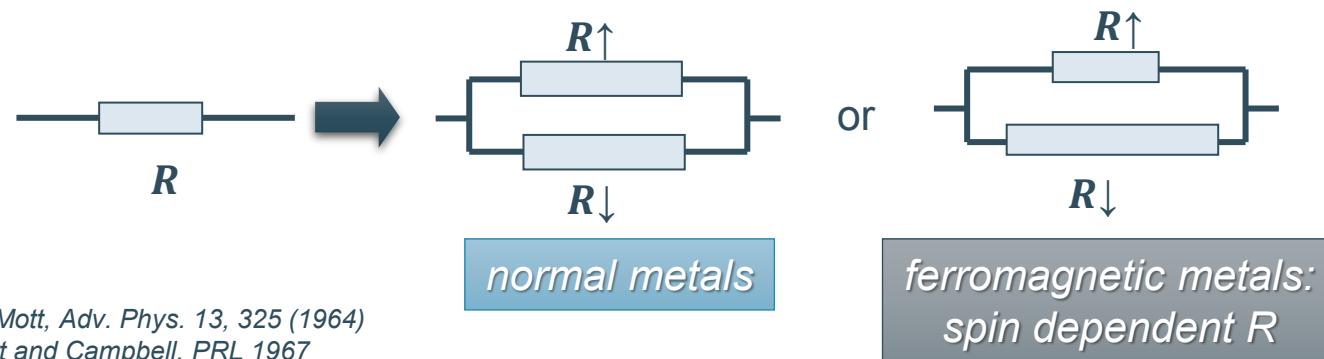
- Fermi "golden rule": **density of scattering probability**  $\propto$  **density of final states**
- This rule states that the scattering probability relates to the density of final states to which the electron can scatter. As a result, in ferromagnetic materials the scattering probability depends on the spin of the electron.
- Ferromagnetic metals (e.g. Fe, Co, Ni and their alloys)
  - "s" and "d" electrons close to the Fermi energy contribute to the electrical conduction but "s" electrons have higher mobility. Therefore, they are the main responsible for the electrical transport.
  - The main scattering effect is the "sd" exchange interaction (i.e. a spin-up "s" electron scatters and occupies a spin-up "d" orbital).
  - The strong difference in density of 3d states at  $E_F$  for spin  $\uparrow$  and spin  $\downarrow$  results in strongly different spin dependent scattering rates. Many empty 3d states for spin  $\downarrow$  imply a large probability of scattering.
  - The change in mean free path translates into changes in the resistivity, such as: mean free paths:  $\lambda_{\downarrow} \ll \lambda_{\uparrow} \rightarrow$  conductivities:  $\sigma_{\downarrow} \ll \sigma_{\uparrow}$



# Spin polarized transport

## Mott model

- This translates into a **different bulk resistivity** for spin-up and spin-down electrons, dependent on the magnetization of the material.
- We assume that the probability of spin-flip scattering is very low.

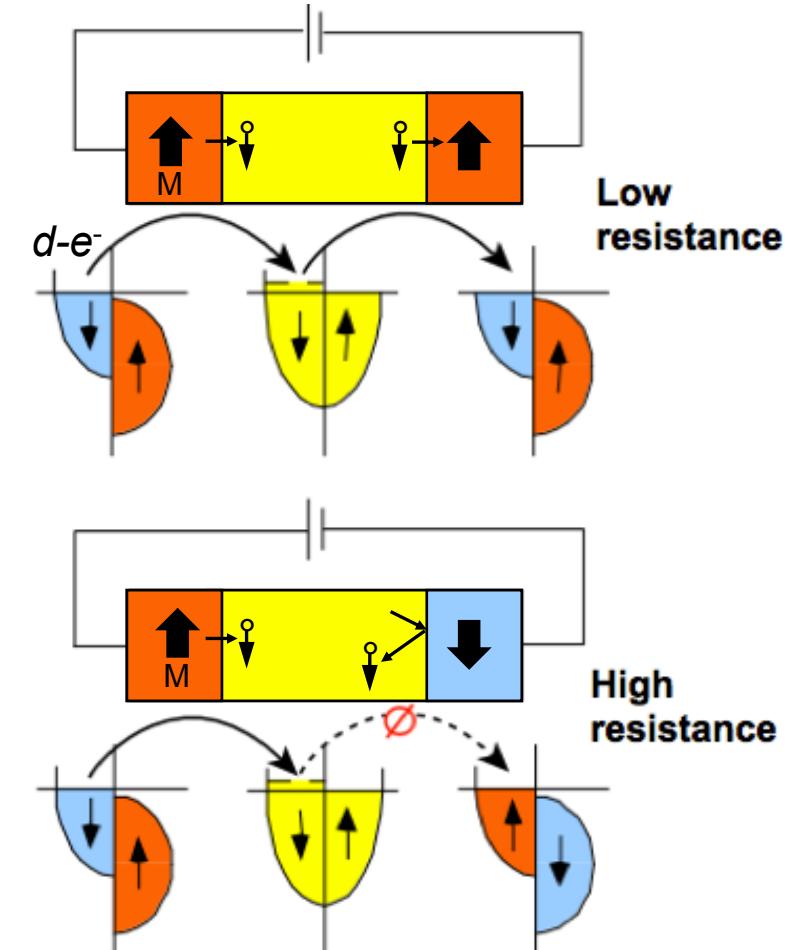


# Giant magnetoresistance



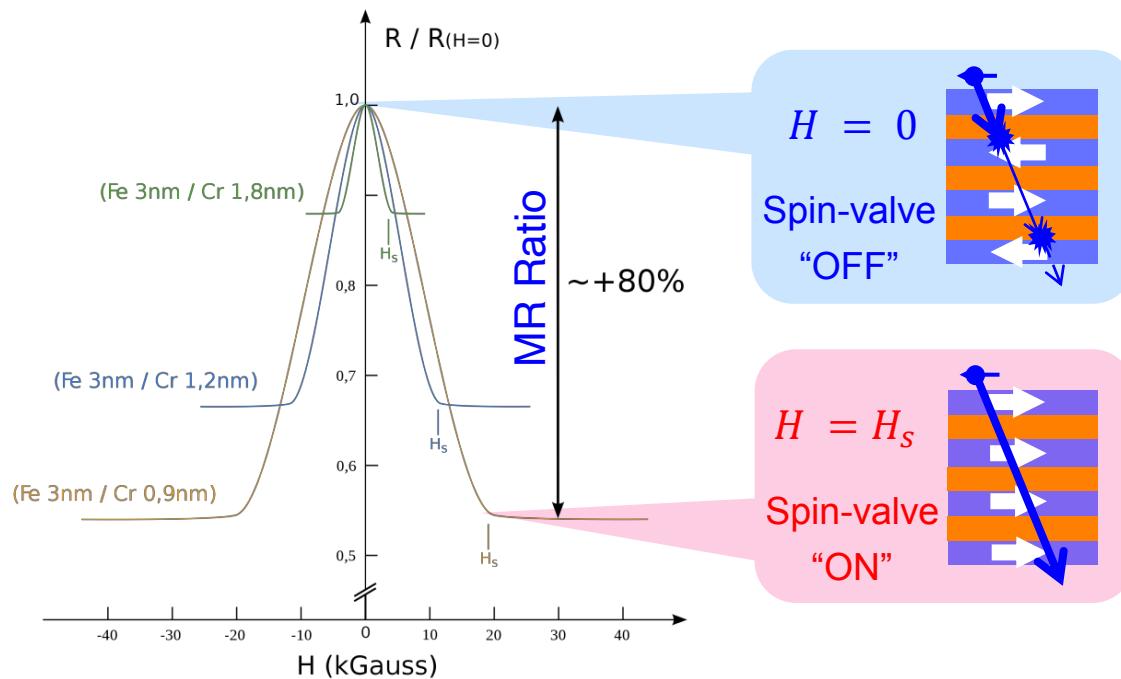
# Spin polarized devices

- The figure illustrates the basic action in a simple spin-polarized device, where it is assumed that the d-electrons are traveling from a ferromagnetic metal, through a normal metal, and into a second ferromagnetic metal.
- In the case where the magnetizations (or, equivalently, the magnetic moments) of the two ferromagnetic metals are in an aligned state, the electrons with the correct spin can freely move from one layer to the next and the resistance is low. When the layers are in the anti-aligned state the carrier movement is blocked at one interface and the measured resistance will be higher.
- In the geometry shown in the figure the current is perpendicular to the plane formed by the interface of the different materials (so-called **current-perpendicular-to-plane** or *CPP* geometry). Actual devices are generally not fabricated in this way, but in the **current-in-plane** (*CIP*) geometry



# Giant magnetoresistance (GMR)

- The CIP geometry makes use of the giant magnetoresistance (GMR) effect in thin magnetic multilayers.



- Like other magnetoresistive effects, GMR is the change in electrical resistance in response to an applied magnetic field. It was discovered that the application of a magnetic field to a Fe/Cr multilayer resulted in a significant reduction of the electrical resistance of the multilayer.
- The change in the resistance of the multilayer arises when the applied field aligns the magnetic moments of the successive ferromagnetic layers. In the absence of the magnetic field the magnetizations of the ferromagnetic layers are antiparallel. Applying the magnetic field, which aligns the magnetic moments and saturates the magnetization of the multilayer, leads to a drop in the electrical resistance of the multilayer.
- This effect was found to be much larger than either ordinary or anisotropic magnetoresistance and was, therefore, called “giant magnetoresistance” or GMR.

# Giant magnetoresistance (GMR)

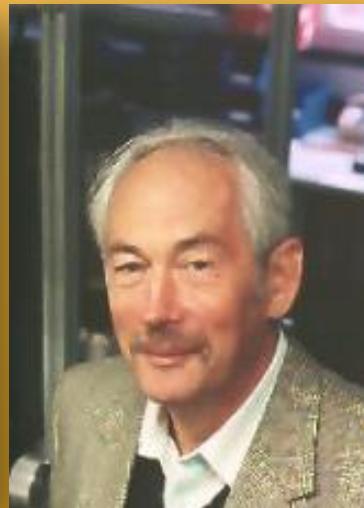
- A very simple resistor model is useful as a starting point for understanding the origin of the current-in-the-plane (CIP) GMR. In this model each metallic bilayer is treated as an independent resistor.
  - If all the magnetic layers are aligned (spin-valve “ON”), there is no strong interface scattering. Hence the whole stack acts as a bulk material (surface scattering is not important) and the resistance measured in the stack is the standard resistance: the GMR is zero.
  - If the magnetic layers are antiparallel (spin-valve “OFF”) thickness of each film is smaller than the **mean free path** of the electrons ( $\lambda$ ), the electrons may scatter strongly at the interface and the resistance of each film is defined by such scattering:

$$\frac{\rho_{\text{thin film}}}{\rho_{\text{bulk crystal}}} = 1 + \frac{3\lambda}{8D} (1 - P) \text{ which is valid for } \frac{\lambda}{D} > 0.3, P = 0 - 1 \text{ (Slides # 46, Chapter 3)}$$

(Then, if the magnetization of each film is the same, the interface scattering is minimized. The material would be equivalent to have a thick conductive film with thickness  $D \gg \lambda$  and the resistance measured for the stack is low. On the other hand, if the magnetization of each magnetic film is opposed to the neighboring films, the material behaves as a stack of thin films with thickness  $D < \lambda$ , in which surface scattering is much higher. Therefore, GMR can be observed.)

# Giant magnetoresistance (GMR)

- This spin polarization effect led to the discovery of the GMR.



Physics Nobel Prize  
2007

1988: GMR discovered simultaneously  
by A. Fert *et al.* (Orsay) and P.  
Grünberg *et al.* (Jülich)

# Spin polarized devices

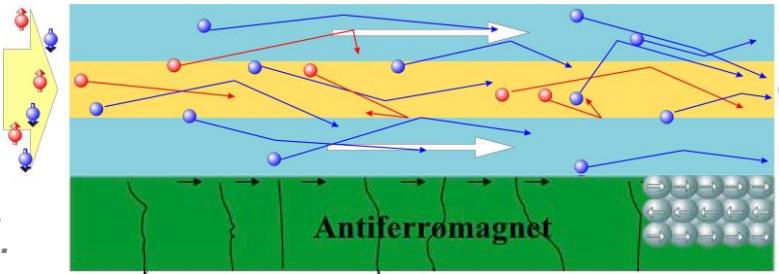


# Hard Disk Drive (HDD) based on GMR

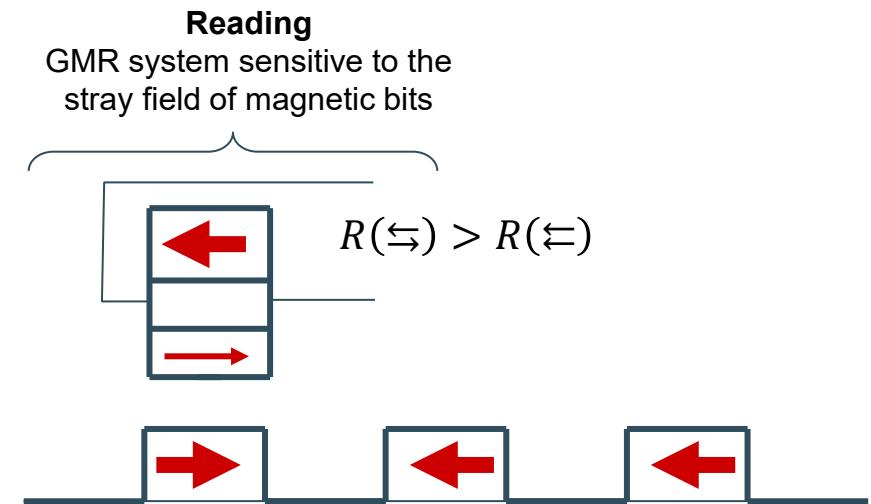
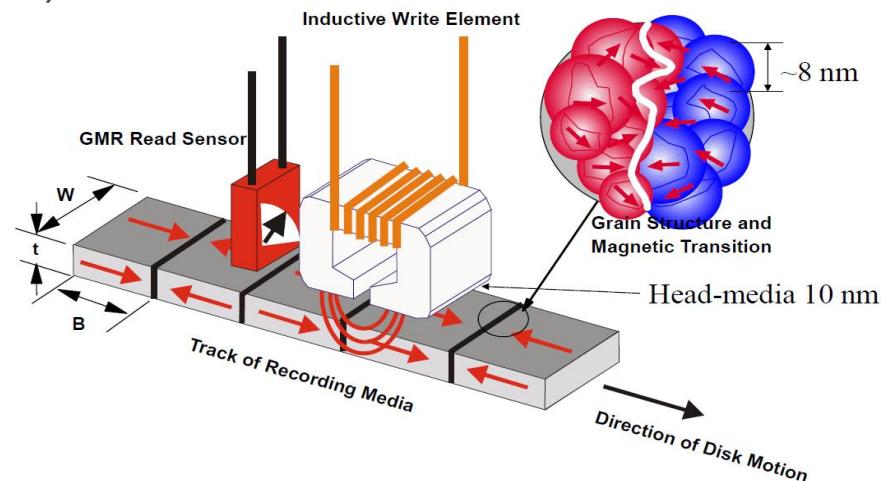
# Spin polarized devices

- GMR: To make a technologically useful device, a “pinning” layer is added to make it harder to change the magnetization of one layer than the other.

*The pinning layer can be a simple layer of an antiferromagnetic material.*



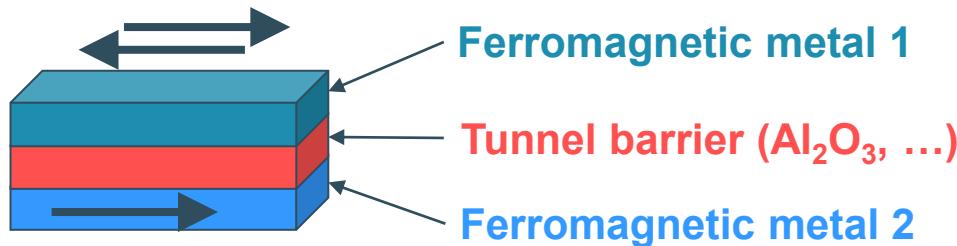
- This structure can be used e.g. to make GMR read heads which have found widespread application in hard disk drives (HDD).



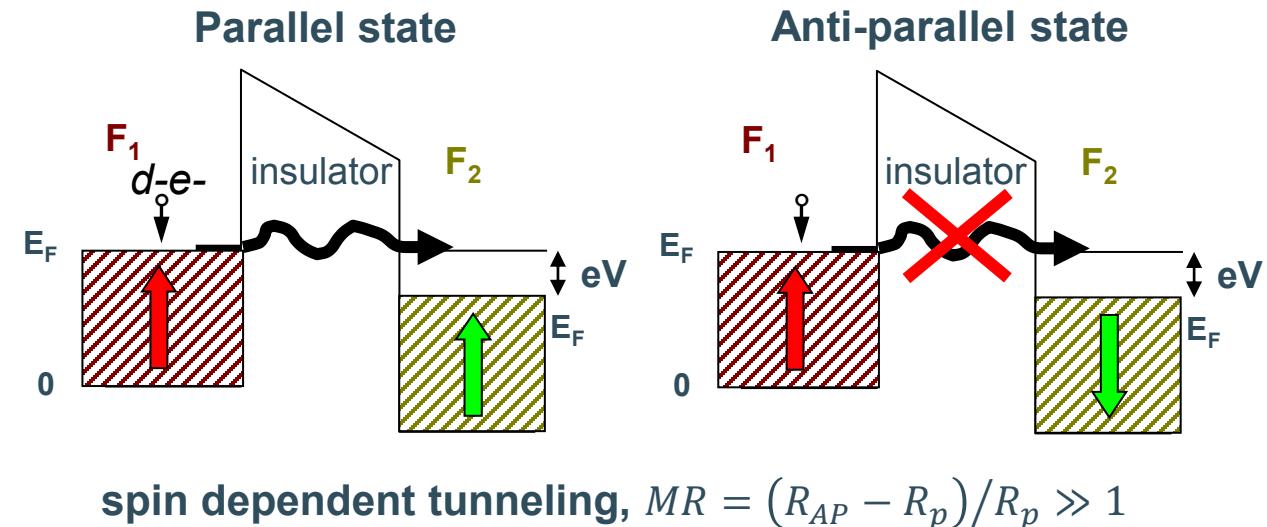
# Magnetic Tunnel Junction (MTJ) and Magnetic RAM (MRAM)

# The Magnetic Tunnel Junction

- A very important structure in spin electronics is the **magnetic tunnel junction** (MTJ).
- It is a magnetic storage and switching device in which two magnetic layers are separated by an insulating barrier (e.g. aluminum oxide, typically 1-2 nanometers thick) allowing an electronic current whose magnitude depends on the orientation of both magnetic layers to tunnel through the barrier when subject to an electric bias.



- The electron spin is not affected by the tunneling.
- The tunneling probability is dependent on the spin.



Claude Chappert, CNRS, France

# The Magnetic Tunnel Junction

- If the magnetic moments of the two ferromagnetic layers are parallel (top figure), spins states with down orientation can be injected from the cathode (M1), and occupy empty down spin states in the anode (M2), leading to a large tunneling current, since:

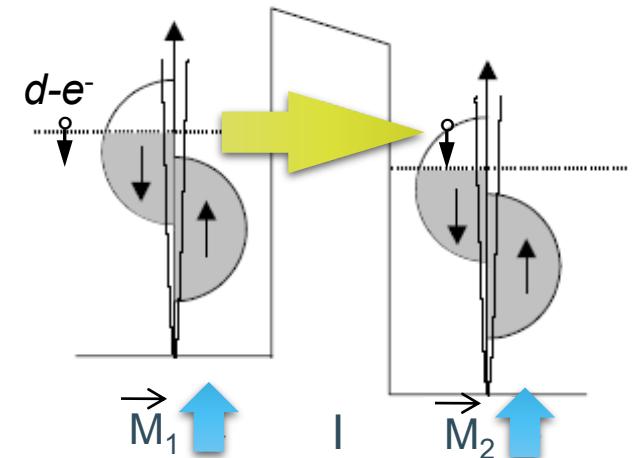
$$J_{\text{tunnel}} \propto T(E, V) f(E_{F,M1}) [1 - f(E_{F,M2})]$$

Tunneling probability

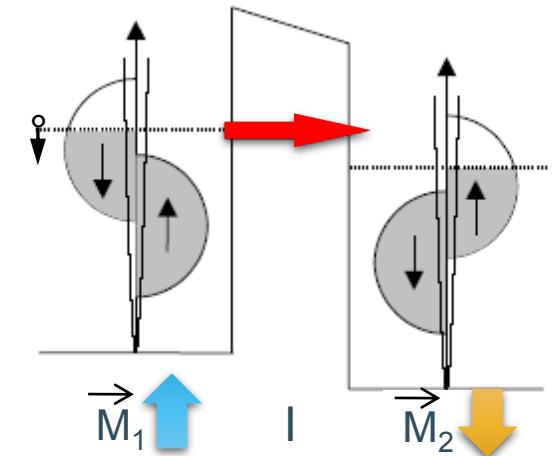
States in M1

Empty states in M2

- The tunneling probability  $T$  depends on the barrier height and thickness of the layer.
- On the other hand, if the magnetic moments of the two ferromagnetic layers are anti-parallel (bottom figure), there are no empty states with down spins available at the anode (M2), and the tunneling current is much reduced.



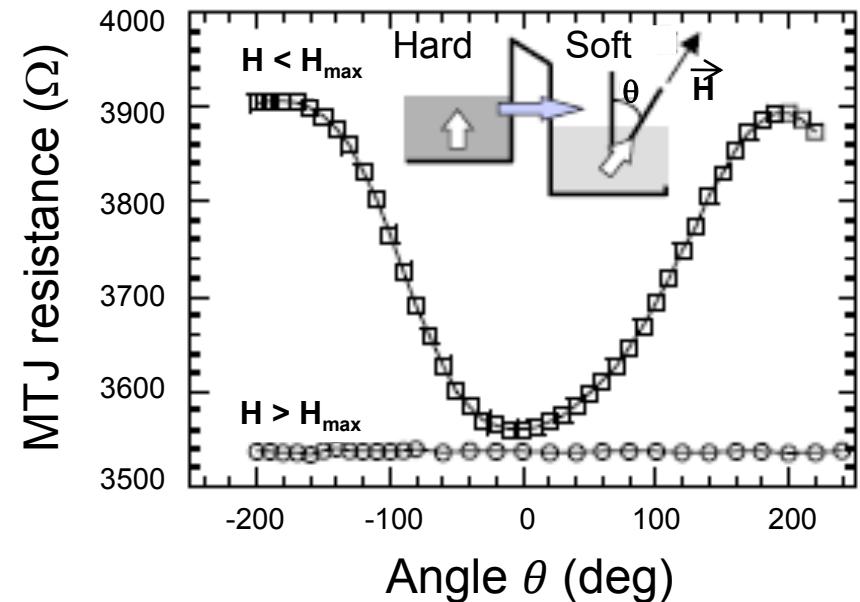
Parallel configuration



Anti-parallel configuration

# The Magnetic Tunnel Junction

- Since such *M1 / Insulator / M2* structure allow the injection of electrons with a specific spin orientation, they are also called “*spin valves*”.
- The resistance of the magnetic tunnel junction can be modulated by changing the orientation of the magnetization of one electrode, with respect to the other, as illustrated in the figure for a  $\text{CoFe}/\text{Al}_2\text{O}_3/\text{Co}$  structure, where the resistance is shown as a function of the angle  $\theta$  between the applied magnetic field and the direction along the magnetization of the CoFe magnetic layer.



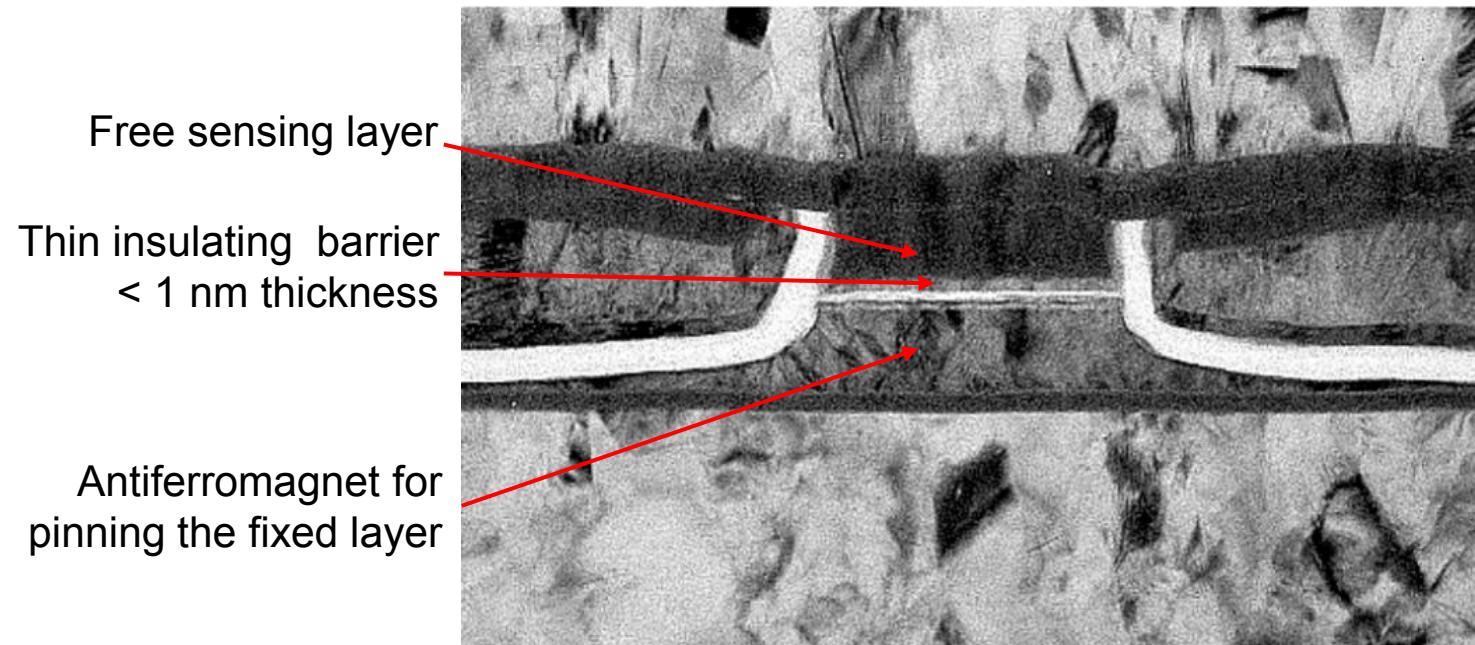
*Resistance of the magnetic  $\text{CoFe}/\text{Al}_2\text{O}_3/\text{Co}$  magnetic tunnel junction as a function of the angle of the applied field for fields below and above the critical value. The resistance varies  $\sim 10\%$  between high and low values.*

# The Magnetic Tunnel Junction

- In the CoFe/Al<sub>2</sub>O<sub>3</sub>/Co structure, the CoFe (M1) layer is a hard-magnetic material, such that it keeps the orientation of its magnetization under the applied magnetic field, for  $H < H_{max}$ .
- The Co layer (M2) is a soft magnet, such that the orientation of its magnetization can be changed under the application of the magnetic field. When  $\theta = 0$ , the magnetizations in M1 and M2 are parallel, and the resistance is low. When  $\theta \sim 180^\circ$ , magnetizations in M1 and M2 are anti-parallel, and the resistance is large.
- When  $H > H_{max}$ , the magnetization of M1 and M2 follows the orientation of  $H$ , and they are always parallel, explaining the low resistance observed in this case.

# The Magnetic Tunnel Junction

- MTJs are used in the write/read head of hard disk drives. As they are more sensitive than write/read heads based on GMR, they allow for a higher information density on the hard disk.

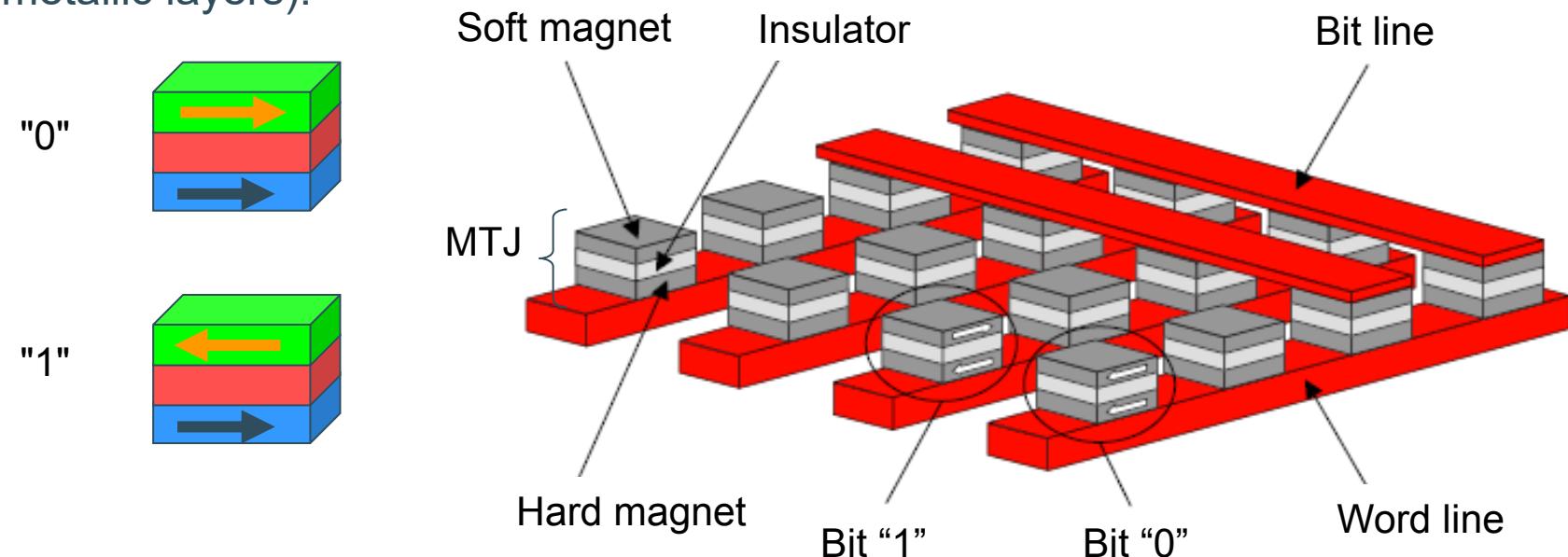


S. Mao, 2005 (Seagate)

- For the tunnel layer typically amorphous oxides such  $\text{TiO}_2$  or  $\text{Al}_2\text{O}_3$  were initially used. Later on, epitaxial tunnel oxides ( $\text{MgO}$ ) were introduced, enhancing significantly the resistance contrast.

# The Magnetic RAM (MRAM)

- Magnetic non-volatile memories can be fabricated by using the spin valve effect. The typical structure of a MRAM (Magnetic Random Access Memory) consists of a series of MTJs, connected by bit lines and a word lines (metallic layers).

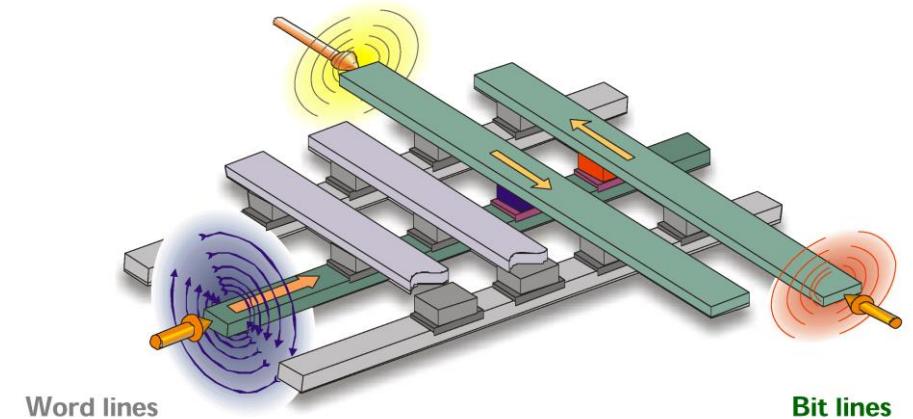


- Principle:
  - store binary information on arrays of magnetic tunnel junctions connected by conducting lines, that serve to address each cell individually for reading and writing
  - writing by sending current pulses in conducting lines

# The Magnetic RAM (MRAM)

- To write the bits of the MRAM, a high current is injected in the *bit* and *word* lines. These currents induce magnetic fields (Ampere's law) that add to each other, leading to a sufficiently high magnetic field to orient the magnetization of the soft magnetic layer in the magnetic tunnel junction.
- The magnetization of the soft magnet compared to the reference layer results in “*low*” or “*high*” values for the resistances of these junctions that can be associated with “1” and “0”.

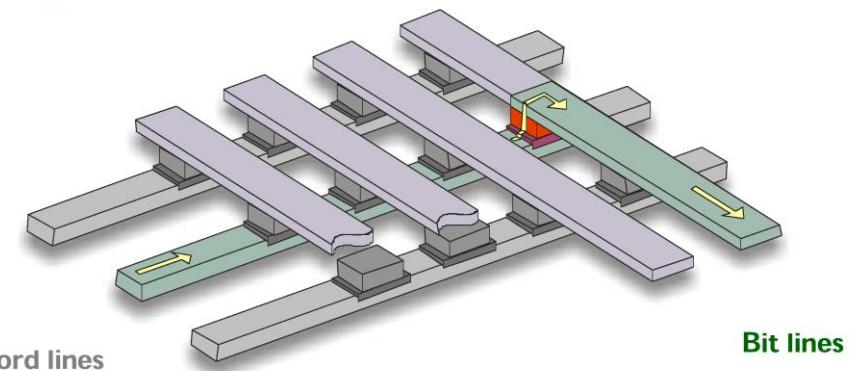
Writing



Word lines

Bit lines

Reading

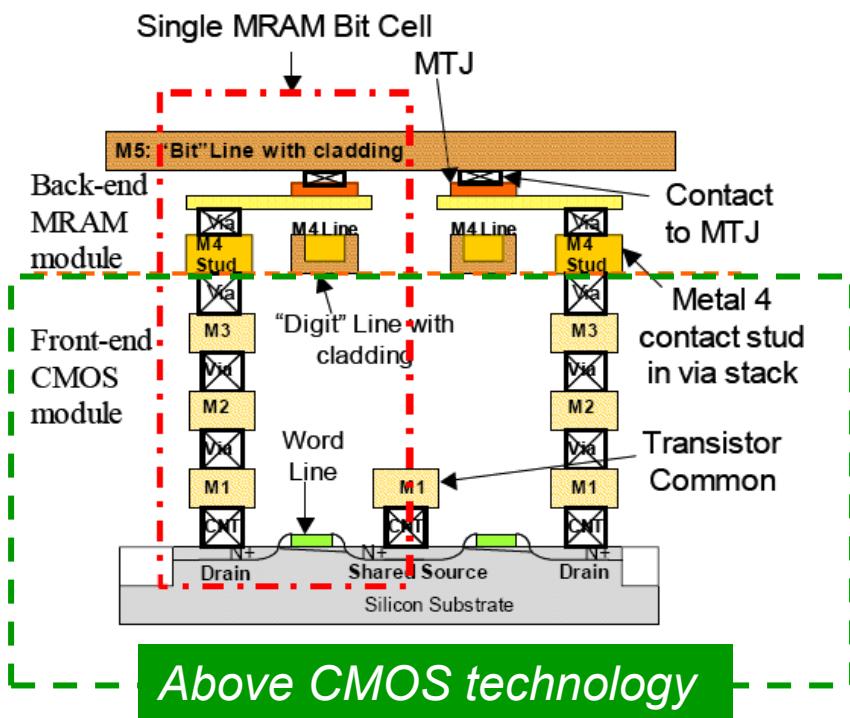


Word lines

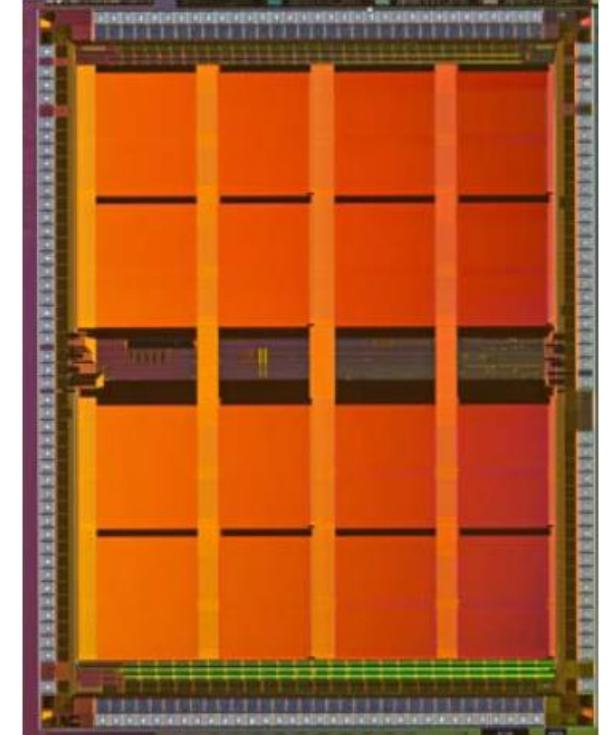
Bit lines

# The Magnetic RAM (MRAM)

- These memories initially received a lot of attention for specific applications as they are very robust and can be made on top of CMOS circuits. However, due to various issues the technology never became a main-stream product.



MRAM made by Freescale. Named "Product of the Year" [Electronics Products Magazine, Jan. 2007]

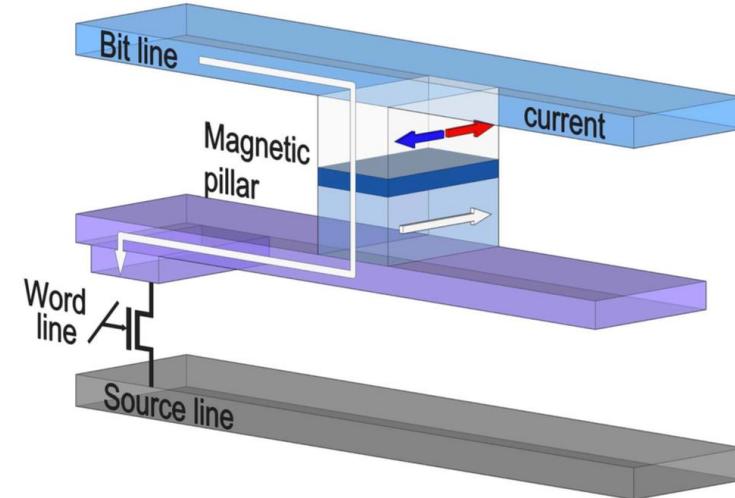
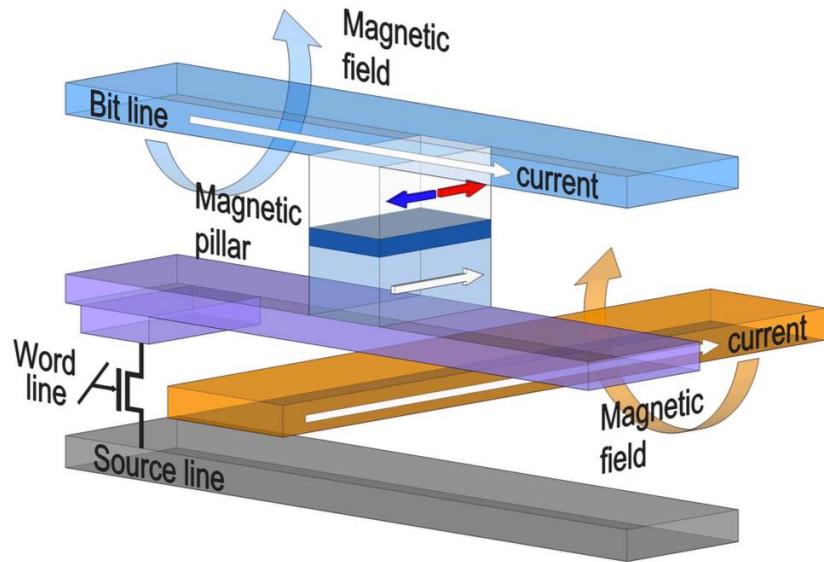


4 Mbit standalone memory  
Toggle switching → reliability,  
speed (30ns), cyclability

# Spin Transfer Torque (STT) and STT MRAM

# From MRAM to ‘spin transfer’ STT-MRAM

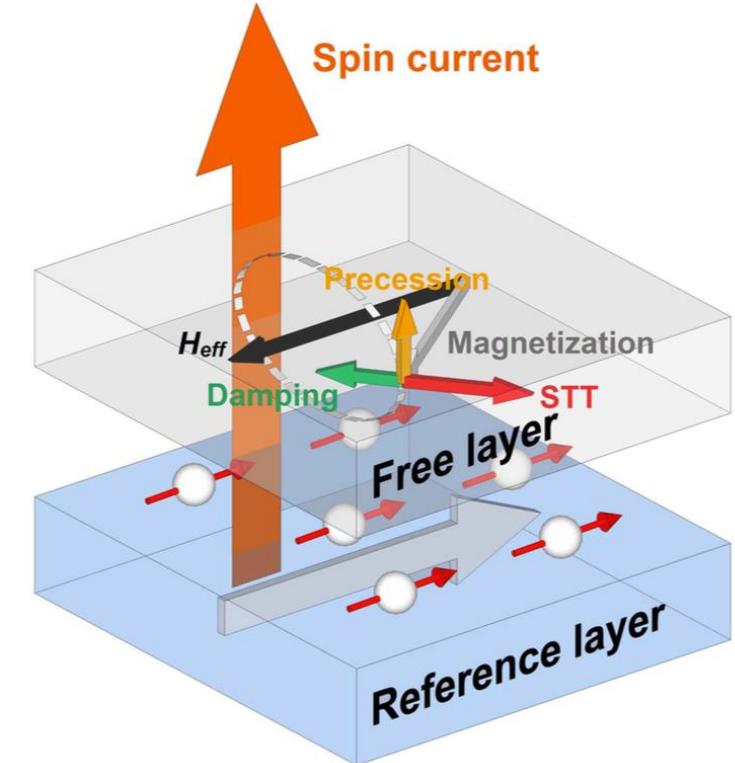
- In conventional field-induced MRAM the write operation is carried out by the current flowing through the wires. The currents generate magnetic fields around the wires. Switching occurs in the cell only, if the magnetic fields from both currents are present at the magnetic pillar.
- In the Spin Torque Transfer Magnetic RAM (STT-MRAM) the switching is obtained by passing a spin polarized current through the tunnel junction. The spin transfer torque effect is used to switch the magnetization of the free layer.



A.Makarov et al, Semiconductor Science and Technology, 31 (2016) 113006

# From MRAM to ‘spin transfer’ STT-MRAM

- **Spin Transfer Torque (STT)** opened a new way of manipulating magnetization dynamics by using spin polarized currents instead of magnetic fields.
- In general, when electrons pass through the thick/hard fixed magnetic layer, the spins of the electrons become aligned with the magnetization of this layer.
- When these spin- polarized electrons enter the free layer (thinner/softer), their spin orientations are getting aligned with the magnetization of the free layer within a transition layer of a few Ångströms. But at the same time, those electrons exert a torque on the magnetization of the free layer by action-reaction, which can cause magnetization switching, if the torque is large enough to overcome the damping.
- Smaller torque values result in magnetization precession around the effective magnetic field.



*Schematic illustration of the spin-transfer torque effect.*

A.Makarov et al, Semiconductor Science and Technology, 31 (2016) 113006

# Spin Transfer Torque (STT)

- In 1935, Landau and Lifshitz have proposed an equation describing the damped motion of the magnetization in a ferromagnet, known as the Landau-Lifshitz (LL) equation. This equation could be used only in a case of small damping. In 1955, Gilbert proposed a modification to the equation which describes the strong damping in the thin films.
- A macro-spin model treats a nanomagnet with the assumption that its internal magnetic degrees of freedom are frozen, so that the dynamics of macro-spin can be phenomenologically described by the Landau-Lifshitz-Gilbert (LLG) equation:

$$\frac{d\vec{M}}{dt} = -\gamma\mu_0(\vec{M} \times \vec{H}_{eff}) - \frac{\alpha\gamma\mu_0}{M_s}\vec{M} \times (\vec{M} \times \vec{H}_{eff})$$

where  $\gamma$  is the gyromagnetic ratio [rad s<sup>-1</sup> T<sup>-1</sup>],  $\alpha$  the dimensionless damping coefficient,  $M_s$  is the saturation magnetization.

- The LLG describes the MRAM switching by magnetic field. In order to be able to describe a switching in STT-MRAM, an additional spin transfer torque (STT) term must be added at the end yielding the Landau-Lifshitz-Gilbert-Slonczewski equation:

$$\frac{d\vec{M}}{dt} = -\gamma\mu_0(\vec{M} \times \vec{H}_{eff}) - \frac{\alpha\gamma\mu_0}{M_s}\vec{M} \times (\vec{M} \times \vec{H}_{eff}) - \beta\vec{M} \times (\vec{M} \times J\hat{m}_f)$$

$\beta$  the coefficient for the STT which depends on both the spin polarization and the geometric configuration between the incoming spin and the local moments in the free layer, and  $J$  the current density. The spin transfer torque counteracts the damping.

# Spin Transfer Torque (STT)

- Landau-Lifshitz-Gilbert-Slonczewski equation:

$$\frac{d\vec{M}}{dt} = -\gamma\mu_0(\vec{M} \times \vec{H}_{eff}) - \frac{\alpha\gamma\mu_0}{M_s}\vec{M} \times (\vec{M} \times \vec{H}_{eff}) - \beta\vec{M} \times (\vec{M} \times \hat{J}m_f)$$

Effective damping

Spin evolution      Excitation term: precessional torque      Intrinsic damping      STT term

$J = J_c$        $J > J_c$

Precession of the spin in switching state for  $J = J_c$  and  $J \gg J_c$ . The blue line shows the trajectory, and the bold arrows show the initial and final states of magnetization. The dotted arrows show an intermediate state of magnetization.

# Spin Transfer Torque (STT)

For switching of the free layer to occur, a critical current is needed to make the spin torque larger than the damping force.

- When  $J$  is small and the spin torque term less than the damping term, the dynamics damp out into an equilibrium state.
- When the spin torque is large enough that it overcomes the intrinsic damping (i.e. larger than the critical current), the effective damping coefficient becomes negative. In this case the deviation from the equilibrium state is amplified and the magnetic moments are switched, which can be detected by a resistance change in the magnetic sandwiched structure, e.g. MTJs or spin-valves.
- When  $J$  and  $H$  satisfy certain conditions, persistent precession of the magnetization can be obtained at a frequency of several GHz. When the precession occurs, the angle between the magnetic moments in the free layer and the pinned layer changes rapidly. Due to the magnetoresistance effect, it gives rise to a resistance change at high frequency; therefore a DC current/voltage induced microwave emission can be observed in the device.

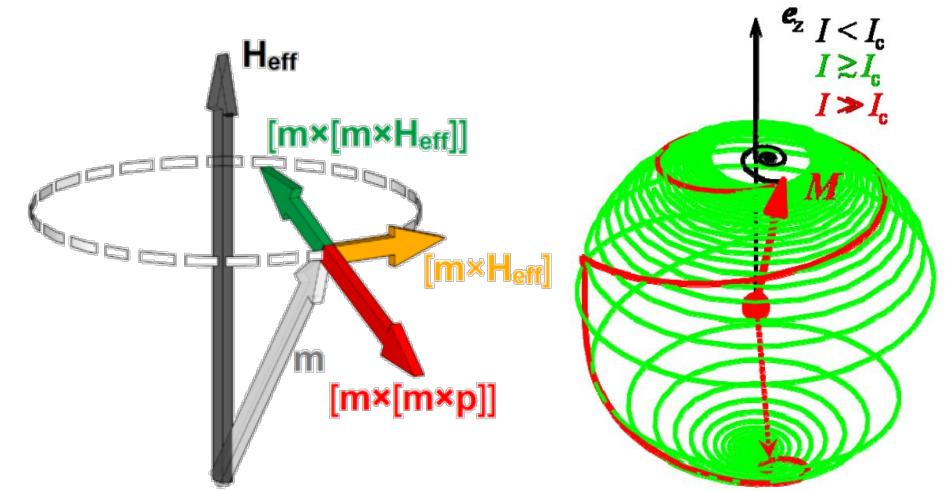
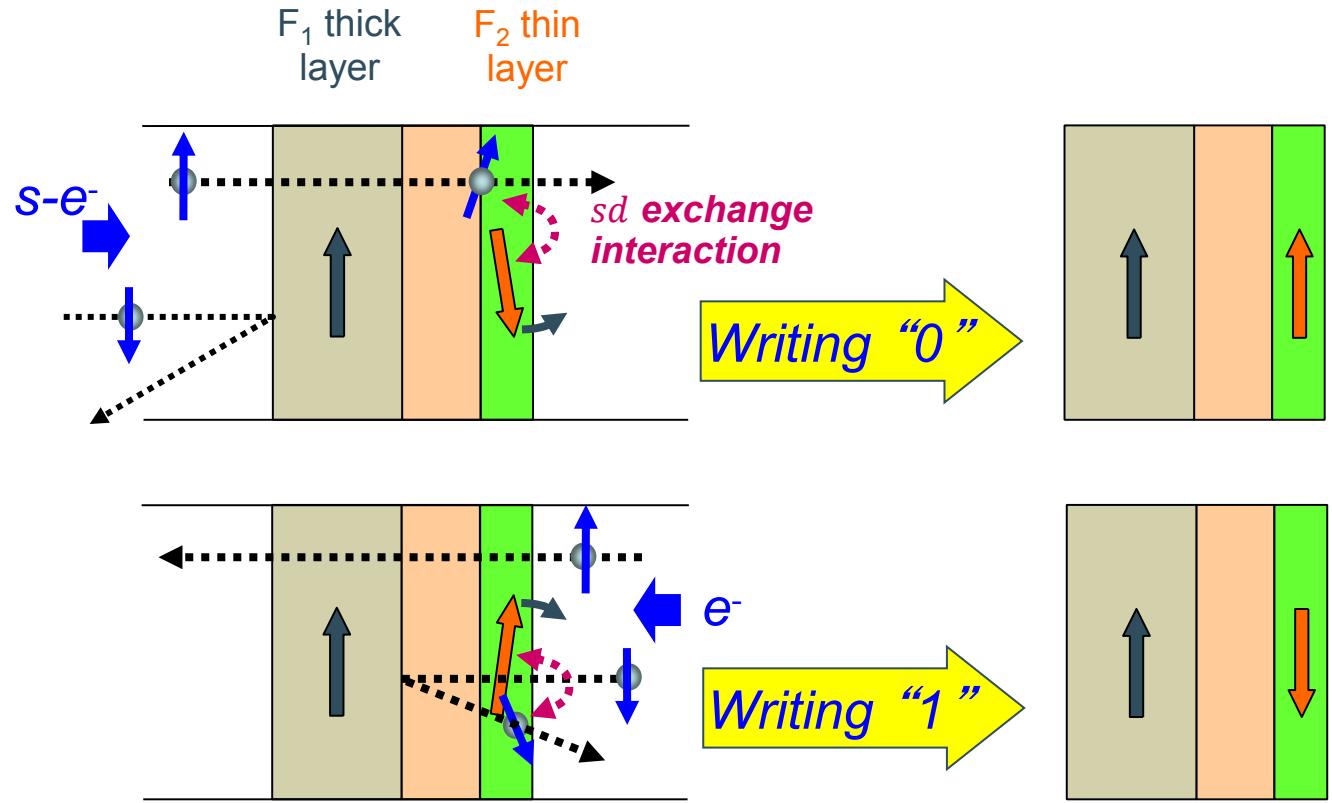


Illustration of the Landau-Lifshitz-Gilbert-Slonczewski equation for a structure with one reference layer and dynamics of the magnetic moments in the free layer (FL) when the damping term is larger, comparable, or smaller than the spin-torque term with various magnitudes of spin polarized current.

# Spin Transfer Torque (STT)

- In this way the spin transfer torque can be used to write a '0' or a '1' into the magnetic memory just by changing the direction of the current flow.



J. C. Slonczewski, JMMM 159, L1 (1996)

Figure illustrating the writing of a '0' or '1' by a bipolar current density  $J_c^+$  and  $J_c^-$

# Magnetic energies for storage

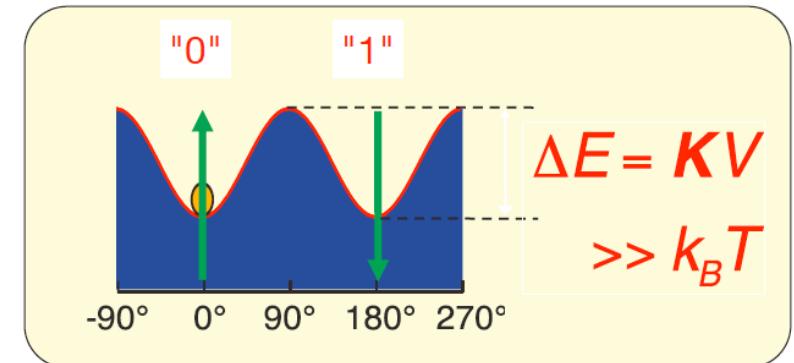
- In order to be useful for non-volatile memory applications, a high thermal (bit) stability is required.
- The stability of the magnetic memory is determined by the magnetic anisotropy energy of the system.
- The volume must be large enough to keep magnetic energy larger than thermal energy. There is a limit in the scaling!!

## **Magnetic anisotropy energy**

total energy changes  
with the orientation of  $\mathbf{M}$



magnetic storage of  
the information



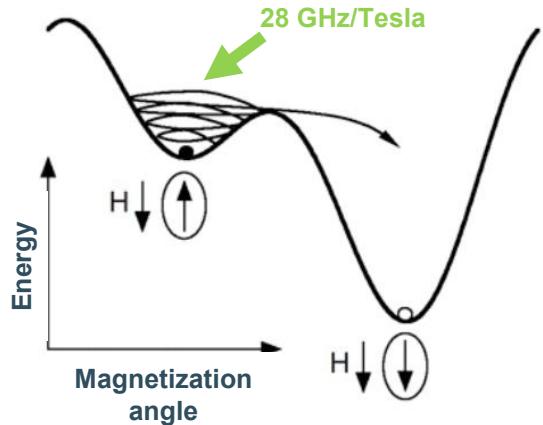
After Thibaut Devolder

# Magnetic energies for storage

- The flipping of magnetization between the two stable states is thermally activated (follows a precession movement). The attempt frequency is function of the material properties and device shape.

- The mean time between two flips is called the Néel relaxation time:

$$\tau = \tau_0 \exp(KV/k_B T)$$



- where attempt time,  $\tau_0 \sim 1 \text{ ns}$

- The long-term stability of the magnetic storage is limited by the spontaneous reversal of the magnetization due to thermal activation.

- To guarantee bit stability for 10 years ( $= 3 \times 10^8 \text{ s}$ ):

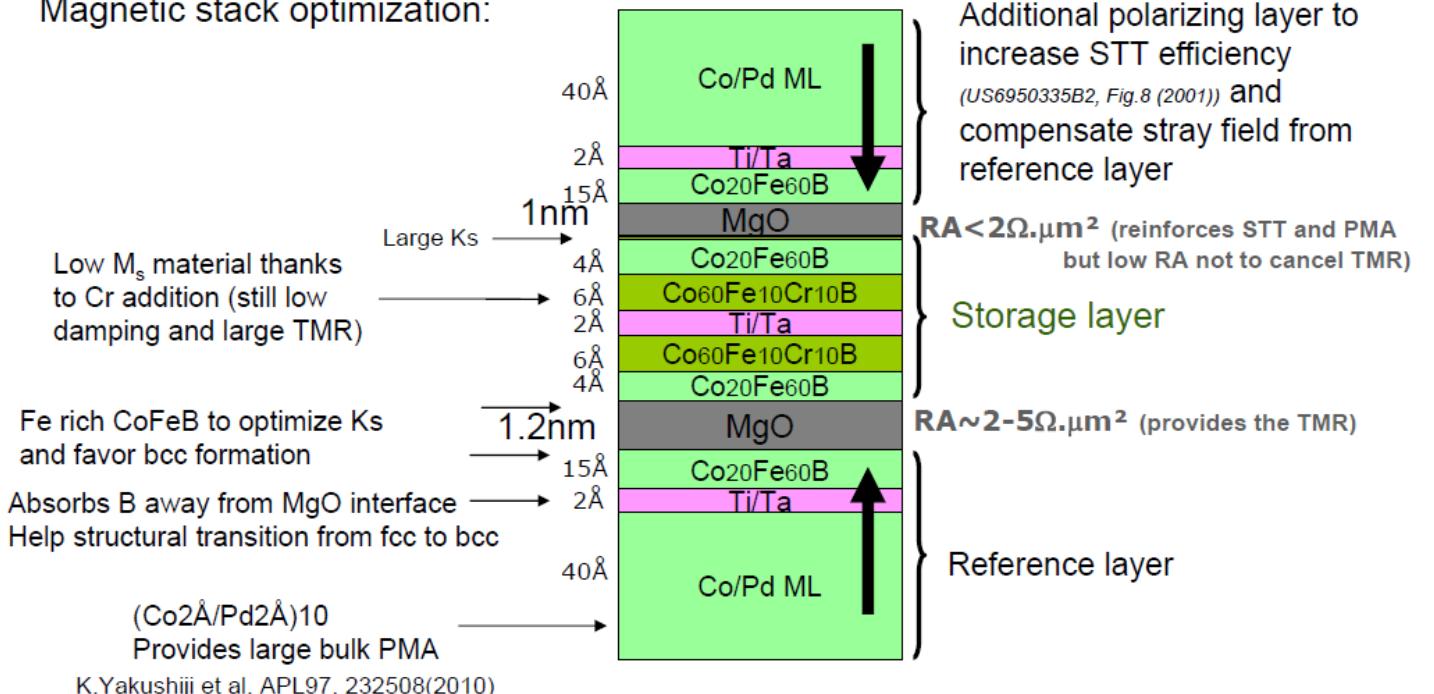
- with error rate ( $1 - P = 10^{-6}$ )  $\Rightarrow KV/k_B T = 54$
      - with error rate ( $1 - P = 10^{-9}$ )  $\Rightarrow KV/k_B T = 68$

- The implication of this is that when one wants to increase the recording density, the bit volume density decreases and material with a higher  $K$  are needed to maintain the stability. On the other hand, increasing  $K$  will increase the energy needed to write the memory. Innovative materials systems will be needed to allow scaling.

# Material stack for p-STT MRAM

- MTJs for STT-MRAMs consist of complex multi-stacks of very thin layers.
- Scalability down to 10nm is expected with currently available materials, making them suitable candidates for fast high-density non-volatile memories.

Magnetic stack optimization:



How small such a stack can be while insuring a 10 year retention?

$$\Delta E = K_{eff}V = [(K_{s1} + K_{s2}) - 2\pi M_s^2 t] \pi R^2 = 70 K_B T \quad \text{with } (K_{s1} + K_{s2}) = 2.9 \text{ erg/cm}^2 \quad \text{and } M_s = 600 \text{ emu/cm}^3$$

⇒ Min diameter = 10 nm still keeping  $\Delta > 70$

Bernard Dieny, CEA, France, IEDM 2011

# Status STT- MRAM



Reverse Engineering ▾

Market Analysis ▾

IP Services ▾

Abc



March 30, 2021



Embedded & Emerging Memory

## World's First 1 Gb 28 nm STT-MRAM Product - by Everspin

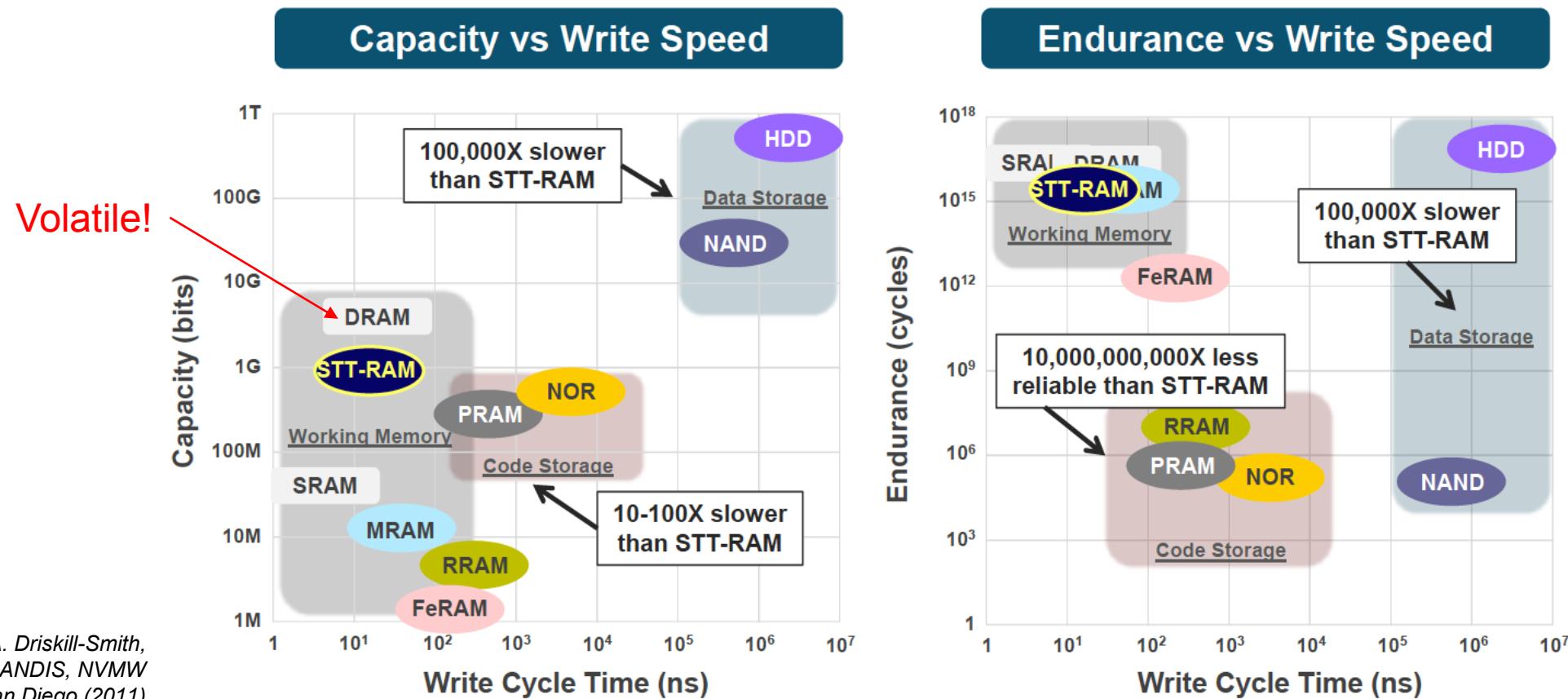
Everspin's new 1-Gigabit (Gb) Spin Torque Transfer Magneto-resistive Random Access Memory (STT-MRAM) device with a 28 nm process is the world's first 1 Gb STT-MRAM product. This 4<sup>th</sup> generation MRAM technology release is a standalone market leader. Its only industry peers, Intel and Micron XPoint Memory, are developing MRAM, ReRAM, and FeRAM memory devices for embedded non-volatile memory (eNVM), rather than discrete emerging memory chips.

According to [Everspin](#), their leading STT-MRAM memory products are being developed for "infrastructure and data center providers to increase the reliability and performance of systems where high-performance data persistence is critical by delivering protection against power loss without the use of supercapacitors or batteries."

Everspin and GlobalFoundries (GF) have been partners since their 40 nm MRAM development and fabrication

# STT-MRAM technology advantages

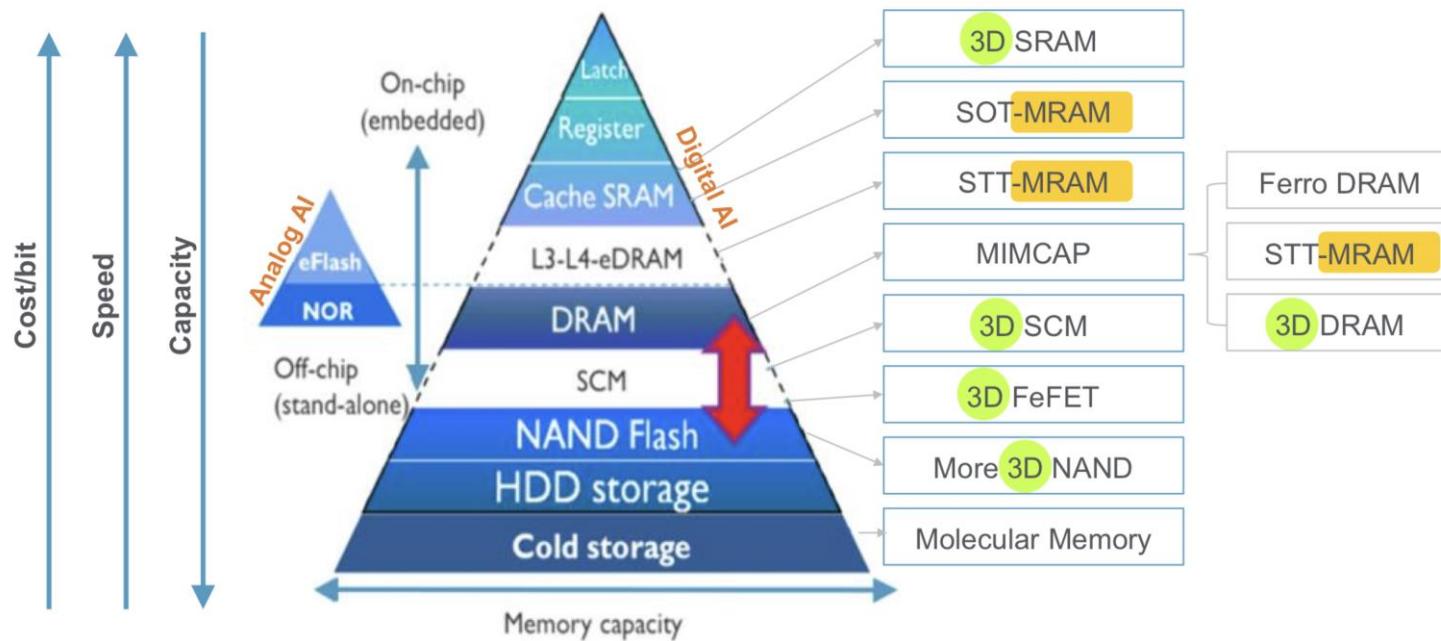
- STT-RAM has the capacity of and speed of working memory (DRAM, SRAM), plus it is non-volatile and has low power consumption.



A. Driskill-Smith,  
GRANDIS, NVMW  
San Diego (2011)

# MRAM application

- Today's systems integrate processors, graphics, as well as memory and storage, often referred to as the memory/storage hierarchy. In the first tier of today's hierarchy, SRAM is integrated into the processor for fast data access. DRAM, the next tier, is separate and used for main memory. Disk drives and NAND-based solid-state storage drives (SSDs) are used for storage.



*"DRAM and NAND are struggling to keep up with the bandwidth and/or power requirements in systems. DRAM is cheap, but it consumes power. DRAM is also volatile, meaning it loses data when the power is shut off in systems. NAND, meanwhile, is cheap and non-volatile (it retains data when the system is shut down). But NAND and disk drives are slow."*

*So for years, the industry has been searching for a "universal memory" that has the same attributes as DRAM and flash and could replace them. The contenders are MRAM, PCM and ReRAM. The new memories make some bold claims. For example, STT-MRAM features the speed of SRAM and the non-volatility of flash with unlimited endurance. Compared to NAND, ReRAM is faster and bit-alterable. And so on.*

*Current and future generations of memories are worth watching. To date, they haven't disrupted the landscape. But they are making a dent against the incumbents in the ever-changing memory market."*

*Emerging memories for pervasive data and compute source*

# Materials Physics and Technology for Nanoelectronics



**Clement Merckling**

clement.merckling@kuleuven.be

imec & KU Leuven (MTM)

Kapeldreef 75, B-3001 Leuven



**Francisco Molina Lopez**

francisco.molinalopez@kuleuven.be

MTM Functional Materials

Kasteelpark Arenberg 44, B-3001 Leuven

# Materials Physics and Technology for Nanoelectronics

## Organic electronics

KU LEUVEN

imec

KU LEUVEN

MATERIAALKUNDE

**Clement Merckling**

clement.merckling@imec.be

IMEC IV, room 2.36

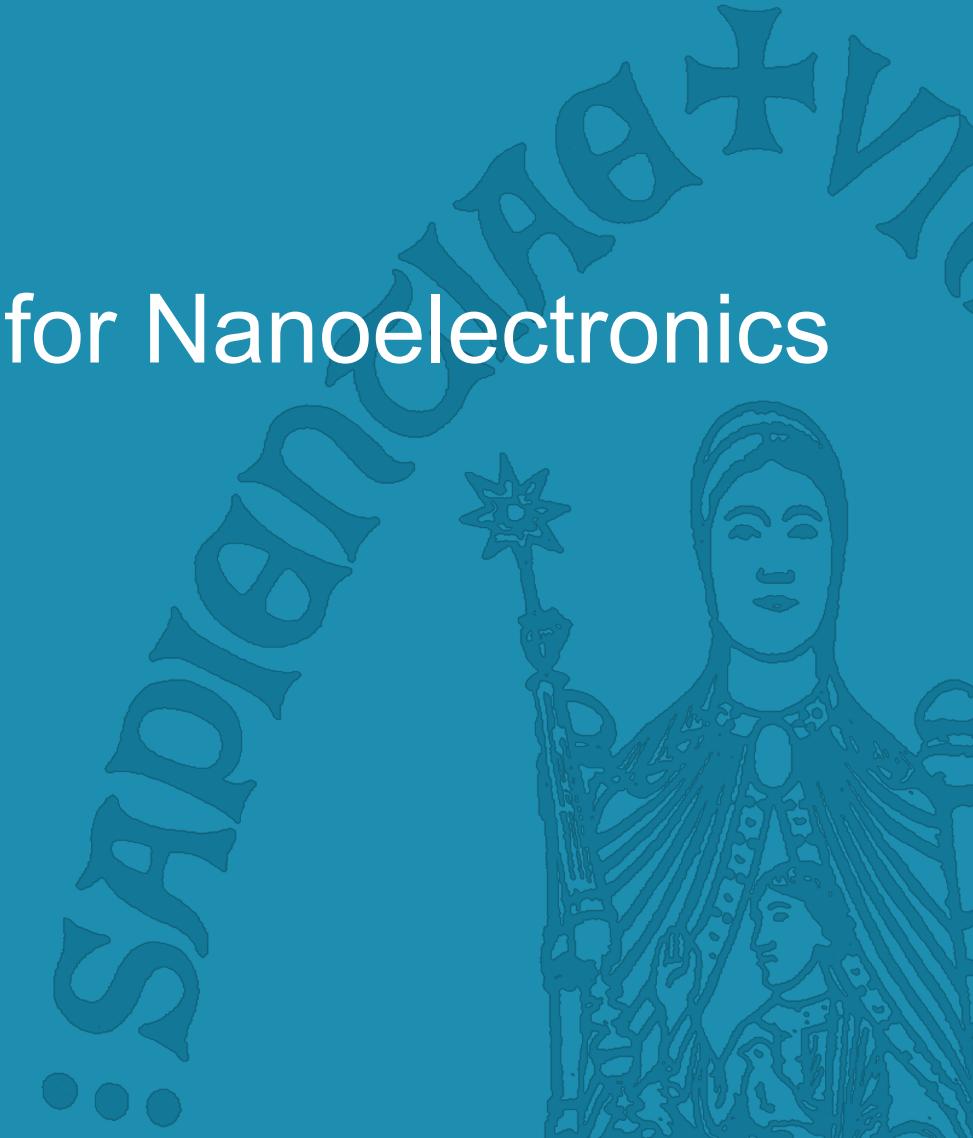
Kapeldreef 75, B-3001 Leuven

**Francisco Molina-Lopez**

francisco.molinalopez@kuleuven.be

Dept. Materials Engineering, room 01.51

Kasteelpark Arenberg 44, B-3001 Leuven



# Outline

- Hybridization
- Electronic structure of conjugated molecules
- Transport in organic electronic materials
- Applications of organic electronic materials



# Hybridization

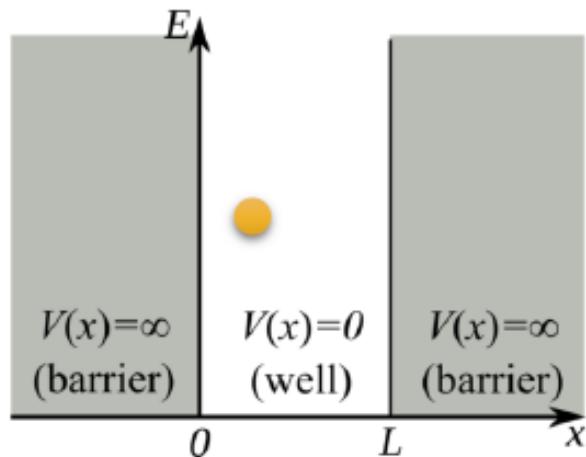


# Hybridization

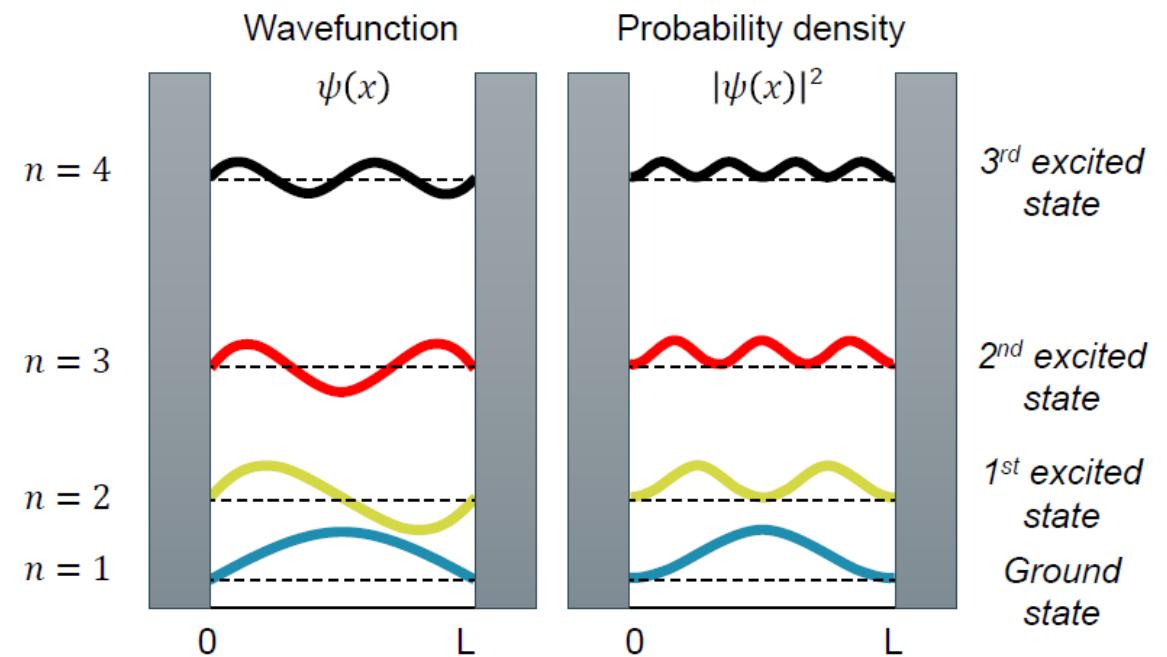
- Atomic orbitals (review from Chapter 2: Solids)

- The **Schrödinger** equation provided the **wavefunction**,  $\Psi(\vec{r}, t)$ , of an electron in an atom, the **probability** of finding it at certain place,  $|\Psi|^2$ , and its quantized **energy**,  $E$ .

Example for 1D potential well (time-independent Schrödinger equation):



$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = E\psi$$

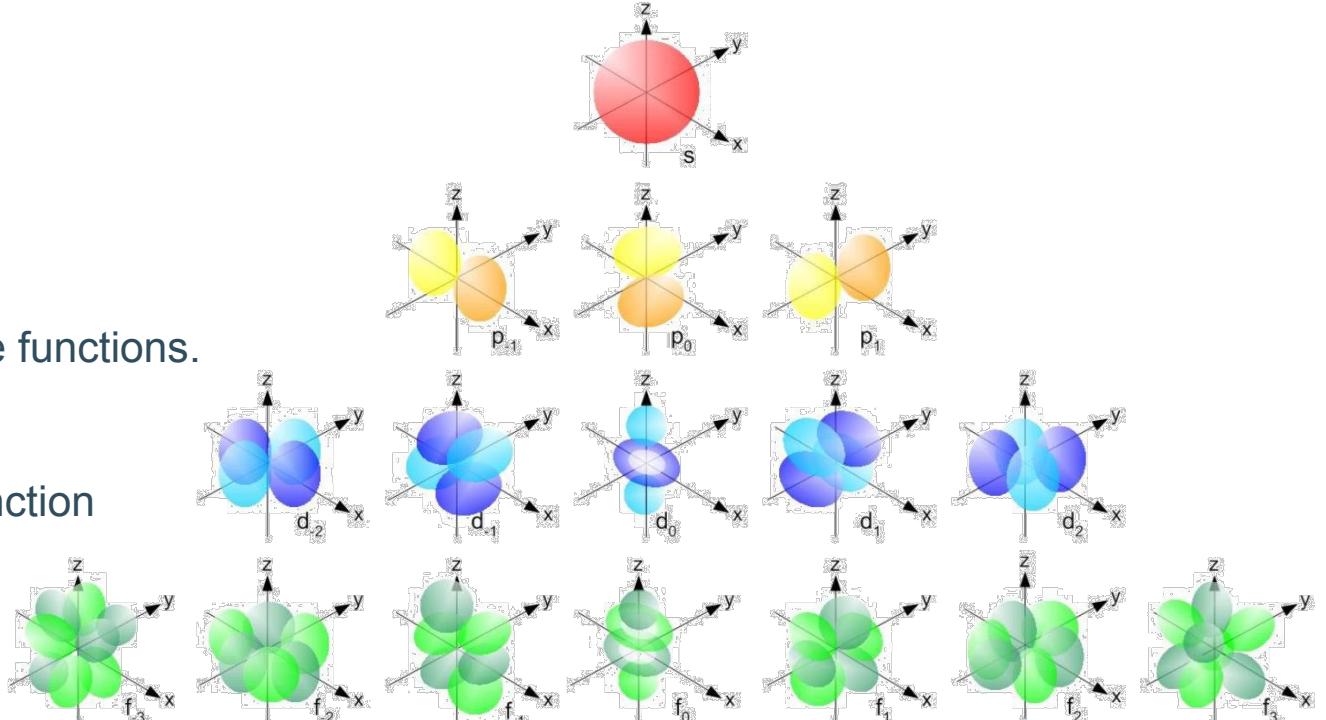


# Hybridization

- Atomic orbitals (review from Chapter 2: Solids)
  - The probability density function  $|\Psi|^2$  in 3D led to the definition of the **atomic orbitals (AO's)** (or zones in the atom where the chances to find electrons are high)

Overview of atomic orbitals shapes of  $s$ ,  $p$ ,  $d$  and  $f$  wave functions.

The color of orbitals represent the phase of the wavefunction (positive or negative amplitude).



# Hybridization

- Molecular orbitals (review from Chapter 2: Solids)

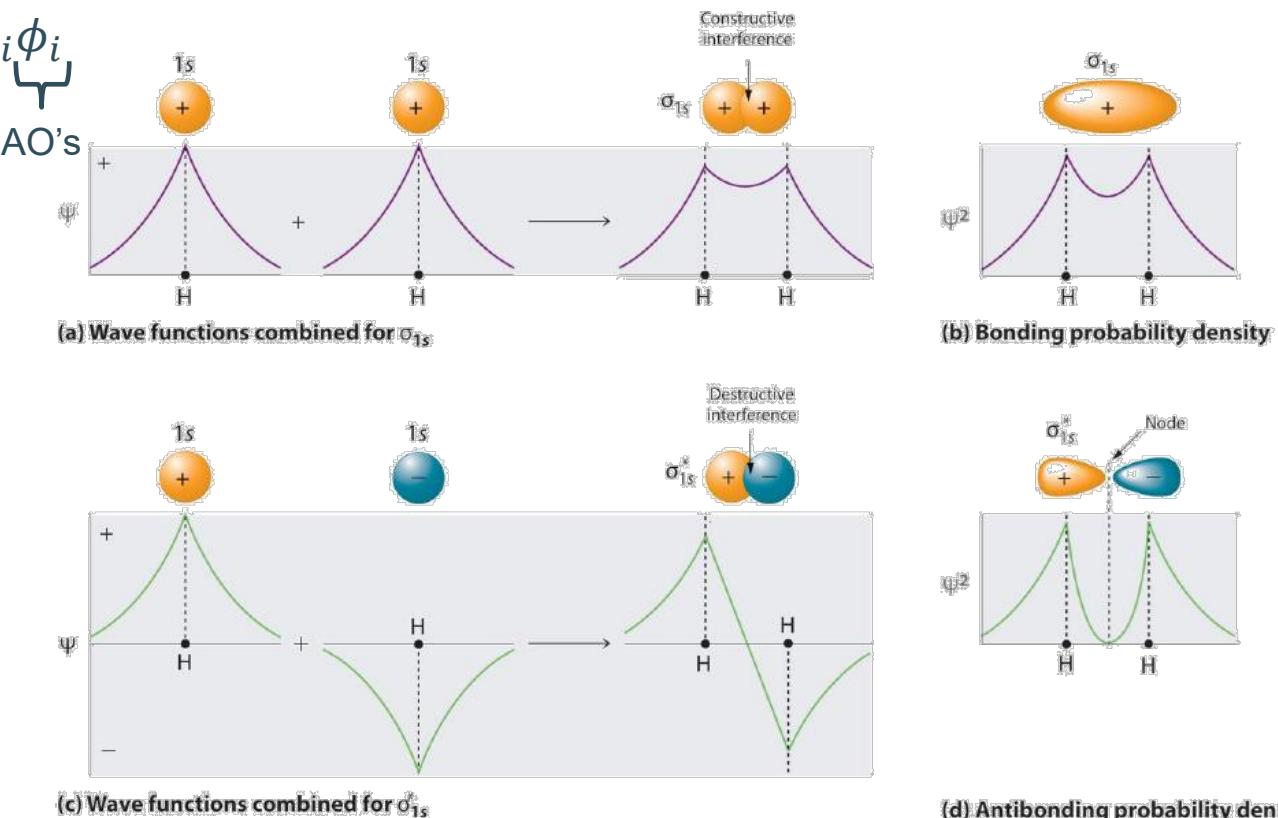
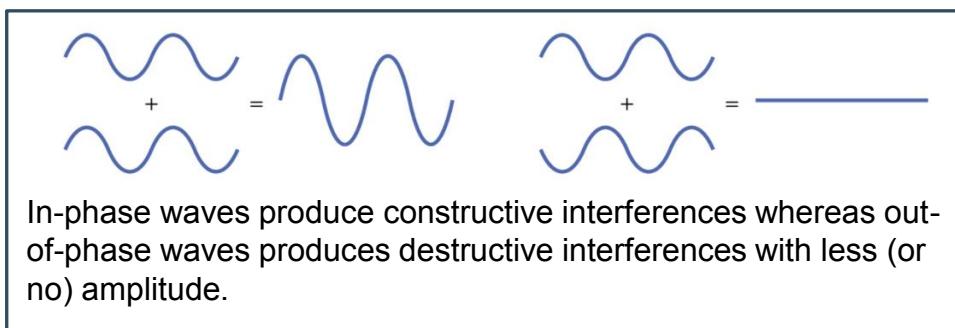
- The solution of the Schrödinger eq. to define molecular orbitals (MO) come from the **linear combination of AO's (LCAO)**:

$$\Psi = \sum u_i \phi_i$$

Example H<sub>2</sub>:

(a), (b) Wavefunctions  $\Psi$  of two H 1s AO and formation of a bonding  $\sigma_{1s}$  MO, probability density  $|\Psi|^2$  of finding the electron in between the two H nuclei is high.

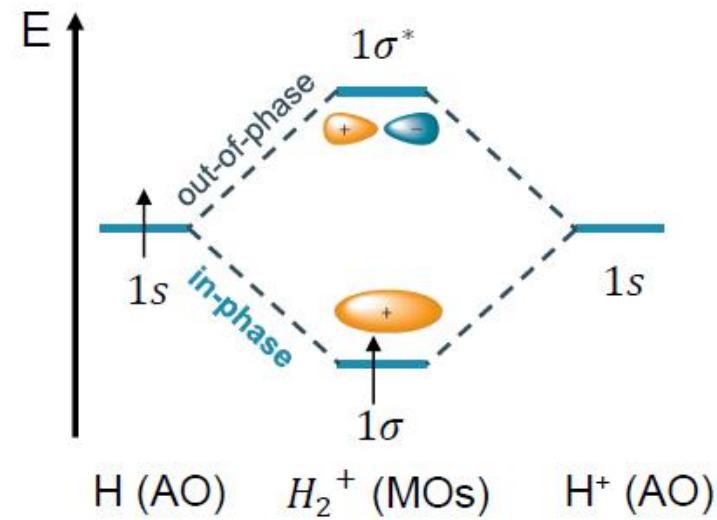
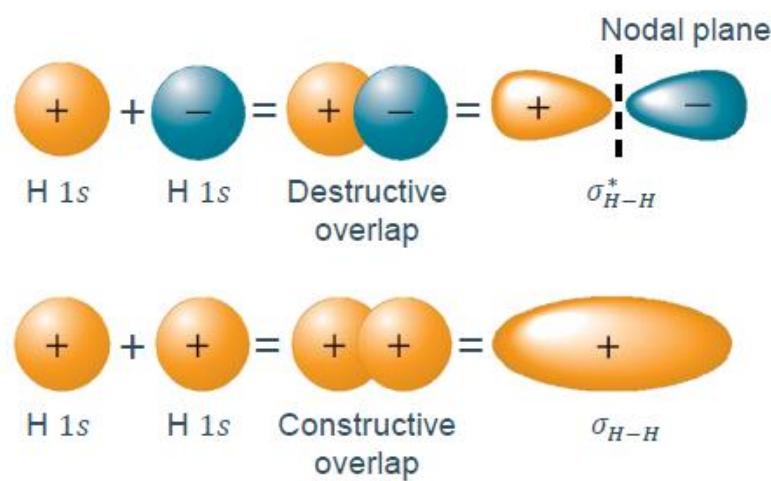
(c), (d) Formation of an antibonding  $\sigma_{1s}^*$  MO, and probability density  $|\Psi|^2$  illustrating the node corresponding to zero electron probability density between the nuclei.



# Hybridization

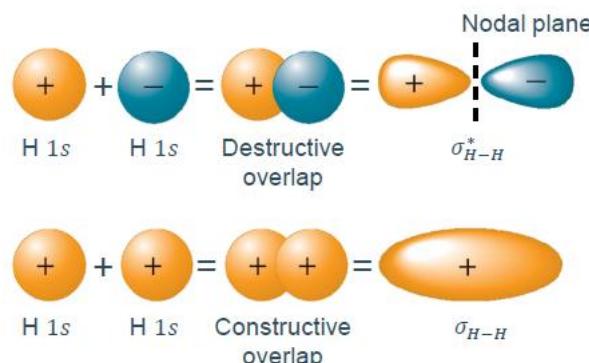
- Molecular orbitals (review from Chapter 2: Solids)
  - The MO's present different **energy** states that depends on whether the **wavefunction** of the electrons from the bonding atoms are **in-phase** or **out-of-phase**

Example of H<sub>2</sub>:

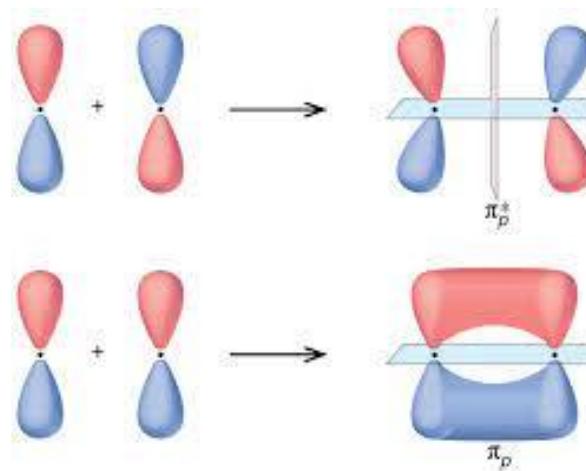


# Hybridization

- Hybridization: Issue of LCAO
  - In the LCAO approach, MO's were built **only from one AO** from each atom.



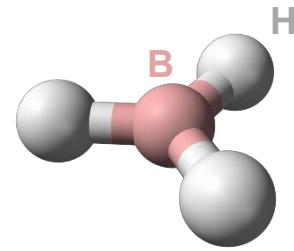
Schematic shapes of bonding and anti-bonding MO's formed by 1s-1s overlap



Schematic shapes of bonding and anti-bonding MO's formed by  $p-p$  overlap

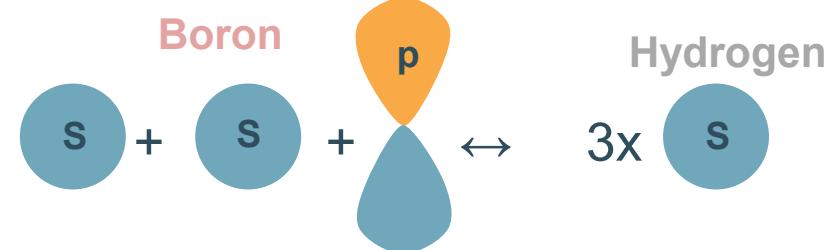
Does this approach correspond to reality?

# Hybridization

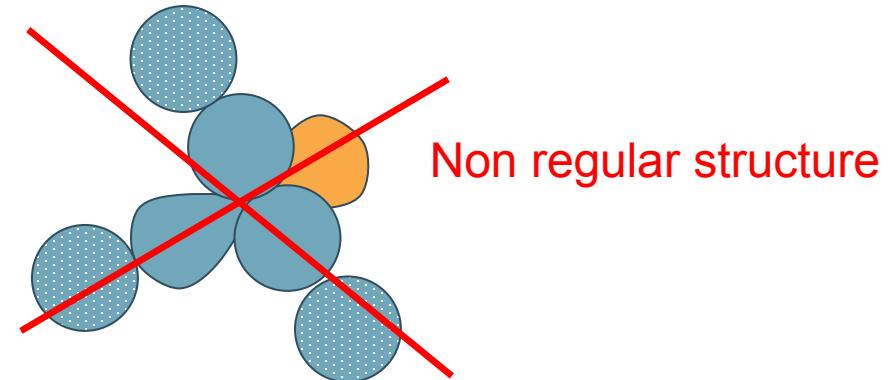
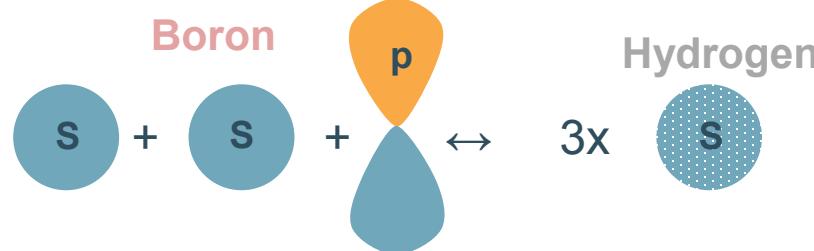


- Hybridization: Issue of LCAO
  - Consider borane (boron trihydride,  $\text{BH}_3$ ):

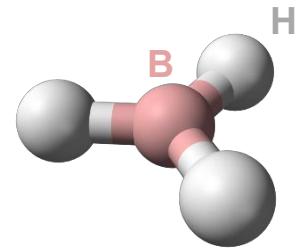
The electronic ground state of B is  $1s^2 2s^2 2p^1$ :



If we assume the MO's being formed from the 3 orbital above, the symmetry of  $\text{BH}_3$  can not be explained!



# Hybridization

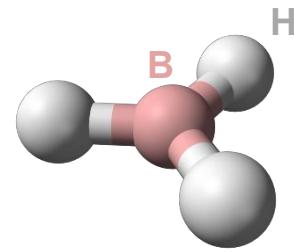


- Hybridization: Issue of LCAO
  - Consider borane (boron trihydride,  $\text{BH}_3$ ):

Greater accuracy can be obtained by using trial wave functions incorporating two or more AOs from individual atoms (forming **hybrid AOs**) as this can lead to MOs of lower energy through increased overlap.

**“Hybridization”** is a mathematical process which is useful in modifying electron densities to allow bonding geometries and electron densities in more complex molecules to be described. The driving force is looking the lowest net potential energy.

# Hybridization



- Hybridization: Explains structure of molecules

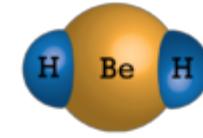
- Consider borane (boron trihydride,  $\text{BH}_3$ ):

Using **hybridization** we can construct three equivalent hybrid AOs for B that explains the regular structure of  $\text{BH}_3$ :



These hybrid AOs extend far from the B nucleus in directions at  $120^\circ$  to each other. The energy cost of creating the hybrid AOs is more than offset by the increased overlap and more negative bond integrals, thereby producing a more stable  $\text{BH}_3$  molecule. Such hybrids are called  **$sp^2$  or trigonal hybrids**.

# Hybridization



- Hybridization: Energy implications
  - Consider, for example, beryllium dihydride ( $\text{BeH}_2$ ):

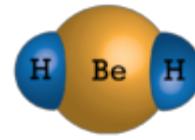


This is known to be a linear molecule (H-Be-H) with an angle of  $180^\circ$  between the two Be-H bonds. MOs to describe the Be-H bonds must be built from the 1s AOs of hydrogen.

The ground state of Be atoms is:  $1s^2 2s^2$

... but constructing MOs for the two Be-H bonds using only 2s AOs of Be yields results for the bond strength and bond length that disagree strongly with experiment.

# Hybridization



- Hybridization: Energy implications

- Consider, for example, beryllium dihydride ( $\text{BeH}_2$ ):

Suppose we instead construct our MOs for  $\text{BeH}_2$  with the following hybrid AOs that also contain  $2p$  AOs (which have energies only slightly higher than the  $2s$  AOs):

$$\phi_1 = \frac{\phi_{2s} + \phi_{2p_x}}{\sqrt{2}} \text{ and } \phi_2 = \frac{\phi_{2s} - \phi_{2p_x}}{\sqrt{2}}$$

(We have chosen  $p_x$  because we define the molecular axis as the  $x$ -axis. The  $\sqrt{2}$  normalizes the functions).

Because the  $2p$  orbitals have a slightly higher energy than the  $2s$  orbitals, these hybrid AOs have a slightly higher energy than pure  $2s$  AOs. But these hybrids extend much farther from the nucleus. This produces more overlap with the  $1s$  orbitals, resulting in a bond integral  $H_{12}$  that is more negative, resulting in a lower total energy (stronger bond).

- The expected energy value is:

$$\langle E \rangle = \frac{\int \psi^* H \psi dV}{\int \psi^* \psi dV} = \frac{\int (u_1 \phi_1^* + u_2 \phi_2^*) H (u_1 \phi_1 + u_2 \phi_2) dV}{\int (u_1 \phi_1^* + u_2 \phi_2^*)(u_1 \phi_1 + u_2 \phi_2) dV} = \frac{2u_1^2 H_{11} + 2u_1 u_2 H_{12}}{u_1^2 + u_2^2}$$

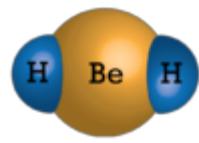
with  $H_{12} = \int \phi_1^* H \phi_2 dV = \int \phi_2^* H \phi_1 dV = H_{21}$

$$H_{11} = \int \phi_1^* H \phi_1 dV = \int \phi_2^* H \phi_2 dV = H_{22}$$

Chapter 2: solids

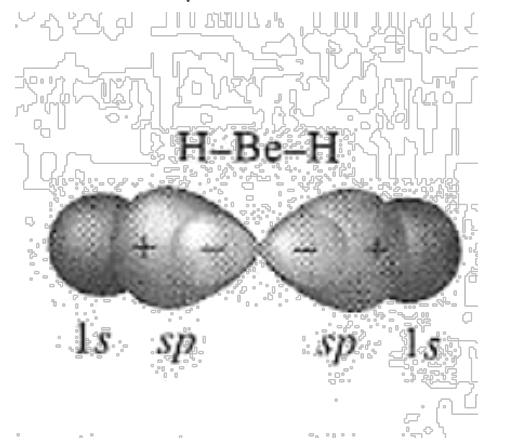
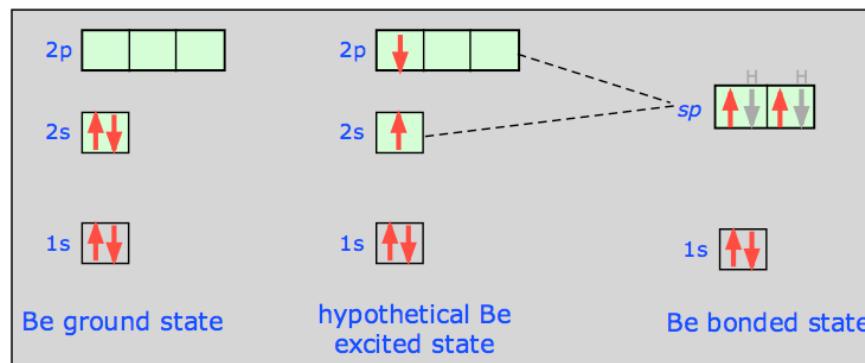
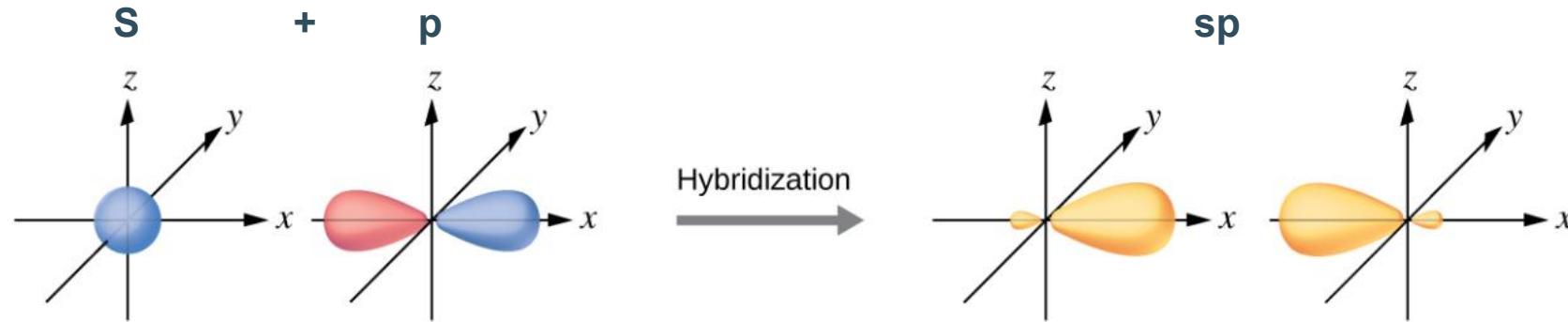
$H_{12} = H_{21}$  is called the *Bond (or resonance) integrals* and  $H_{11} = H_{22}$  the *Coulomb integrals*

# Hybridization



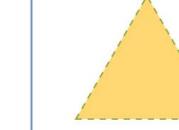
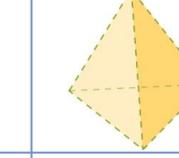
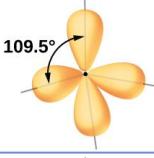
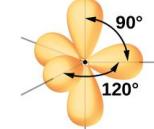
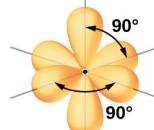
- Hybridization: Energy implications

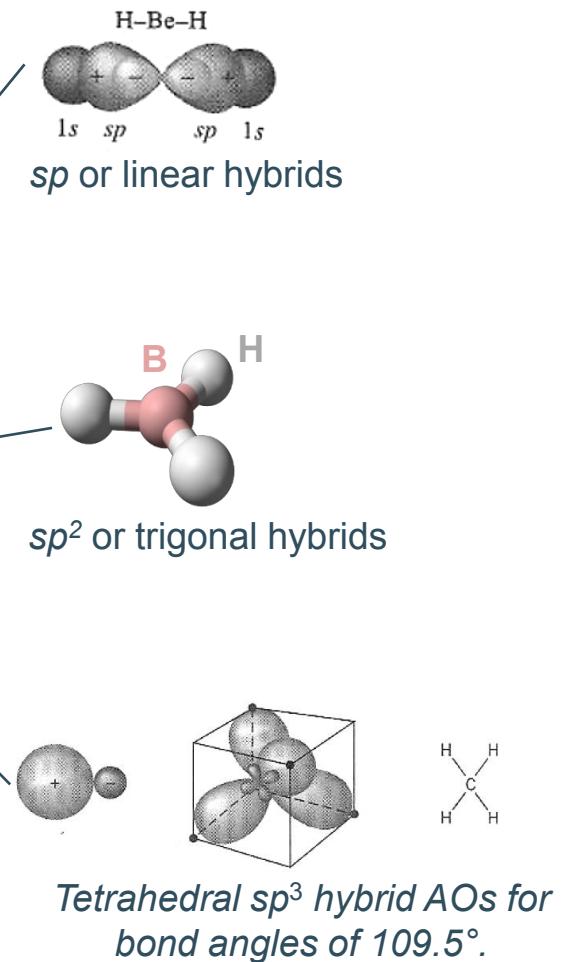
- Consider, for example, beryllium dihydride ( $\text{BeH}_2$ ):  $\phi_1 = \frac{\phi_{2s} + \phi_{2p_x}}{\sqrt{2}}$  and  $\phi_2 = \frac{\phi_{2s} - \phi_{2p_x}}{\sqrt{2}}$



# Hybridization

- Hybridization: summary

| Regions of Electron Density | Arrangement  | Hybridization        |   |
|-----------------------------|--|----------------------|---|
| 2                           | -----  | linear               | $sp$         |
| 3                           |    | trigonal planar      | $sp^2$       |
| 4                           |    | tetrahedral          | $sp^3$       |
| 5                           |   | trigonal bipyramidal | $sp^3d$     |
| 6                           |  | octahedral           | $sp^3d^2$  |



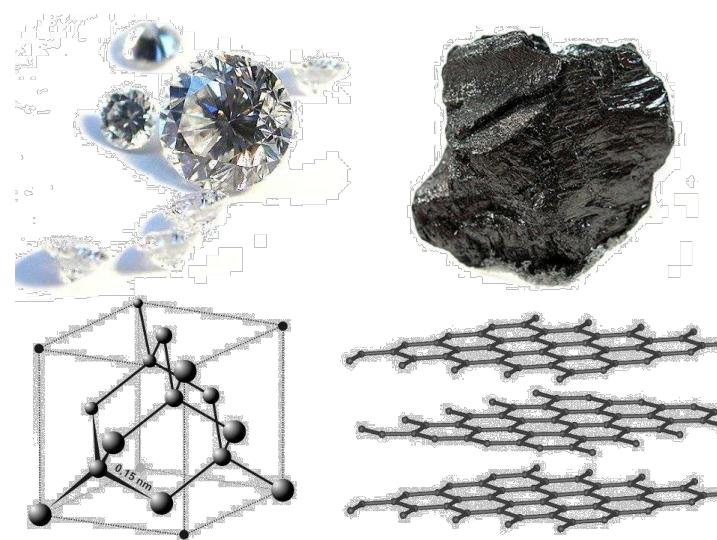
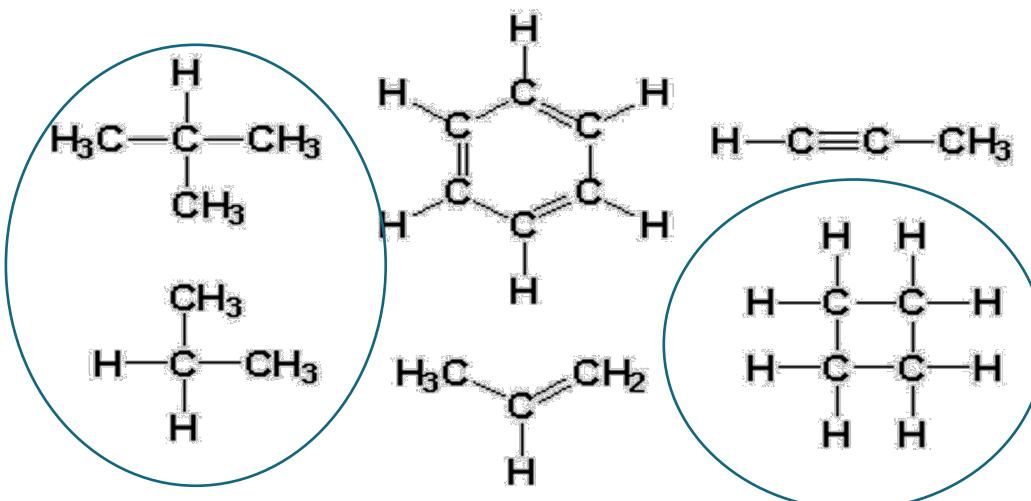
Local symmetries associated with hybrids containing s, p and d AOs.

# Hybridization

- Hybridization: The versatile bonding of Carbon

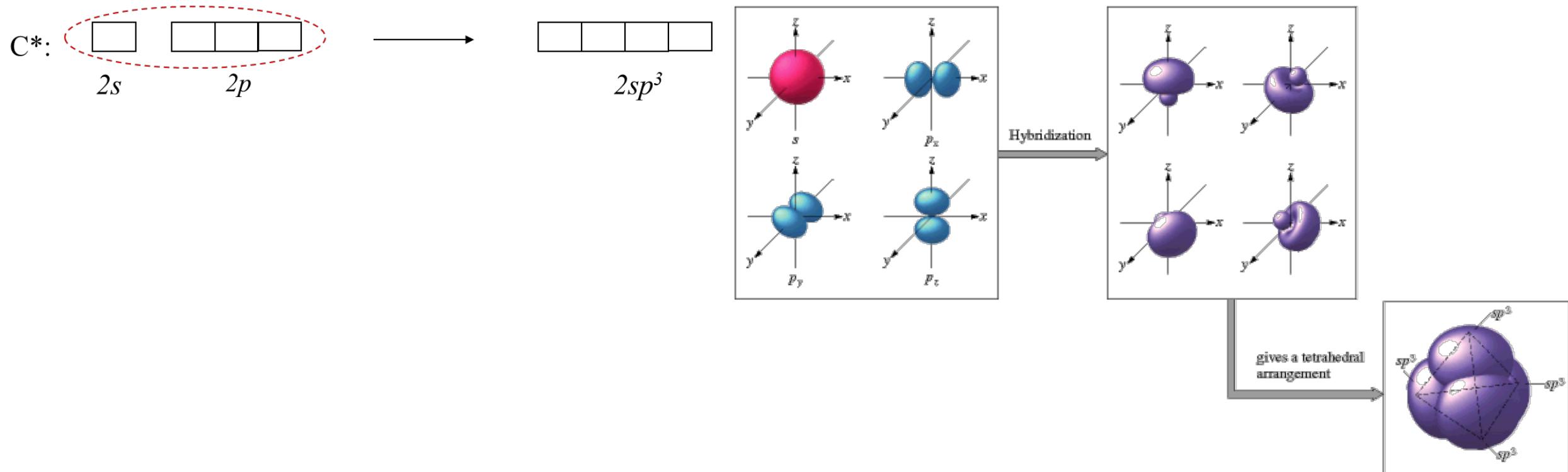
- The four valence electrons of carbon ( $Z = 6$ ), combined with various degrees of hybridization, give carbon a great versatility in bonding. This versatility is responsible for the richness of organic chemistry.

- In many molecules, carbon uses  $sp^3$  hybridization to form bonds with four other atoms. Such molecules are said to be saturated.



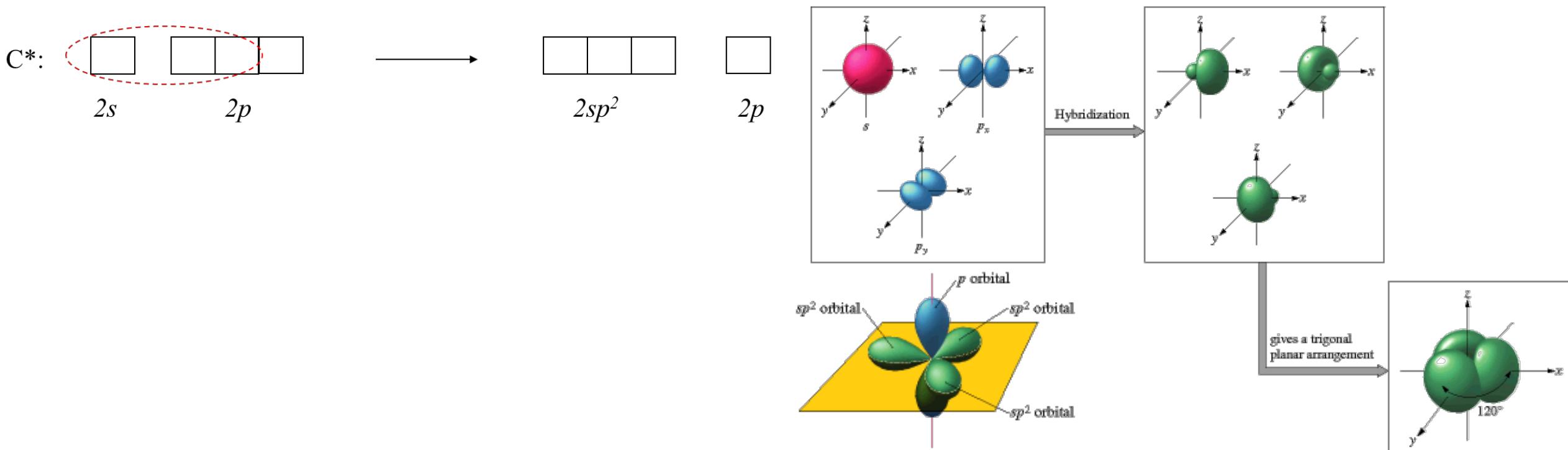
# Hybridization

- Carbon hybridization:
  - $sp^3$  hybridization → linear combination of a  $s$  and 3  $p$  orbitals.



# Hybridization

- Carbon hybridization:
  - $sp^2$  hybridization → linear combination of a s and 2 p orbitals.



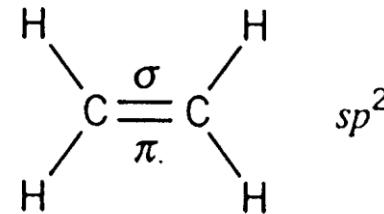
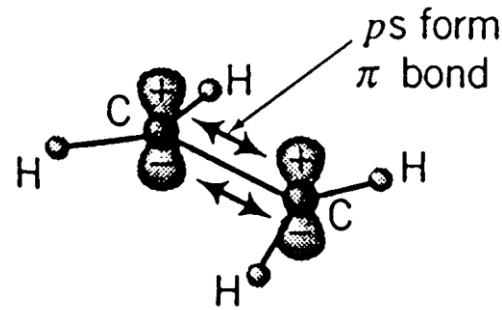
# Hybridization

- Carbon hybridization:

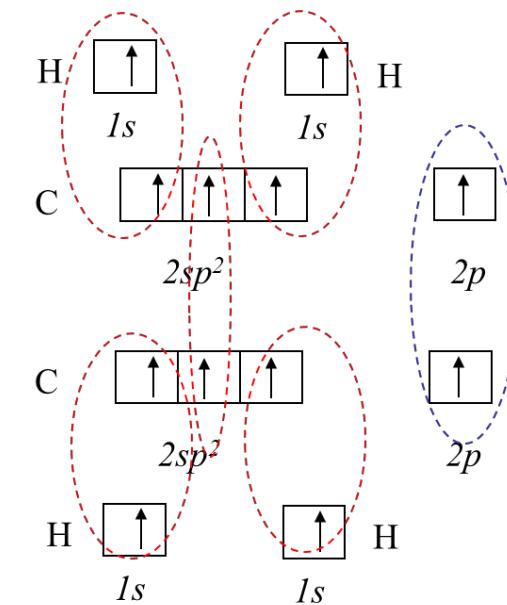
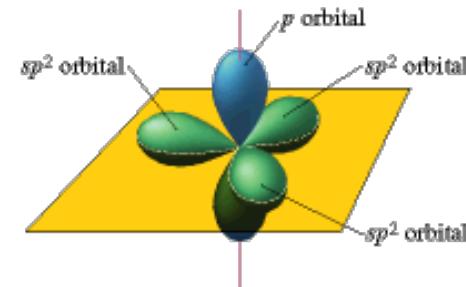
- $sp^2$  hybridization → Example for ethylene.

This molecule is planar, and each carbon has only three neighbors, with two C-H bonds and one C-C bond. The one  $2p$  AO on each carbon, extending out of the molecular plane, **forms a  $\pi$  bond** with the corresponding  $2p$  AO on the other carbon. The C-C bond is therefore a **double bond**, consisting of one  $\sigma$  bond ( $sp^2-sp^2$ ) and one  $\pi$  bond ( $p-p$ ).

Formation of 5  $\sigma$  bonds and 1  $\pi$  bond, with a double C=C bond (bond length: 1.34 Å)

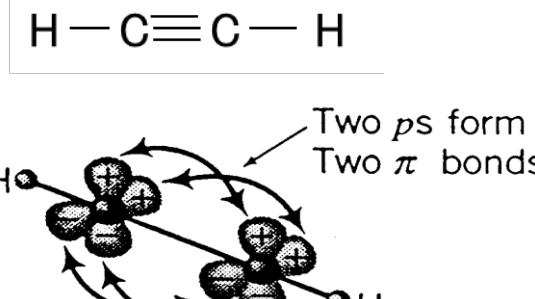
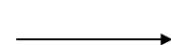
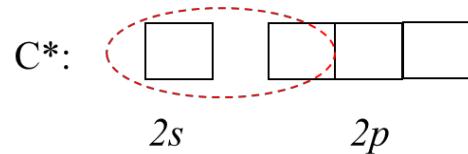


Ethylene, a planar molecule with a double C-C bond.

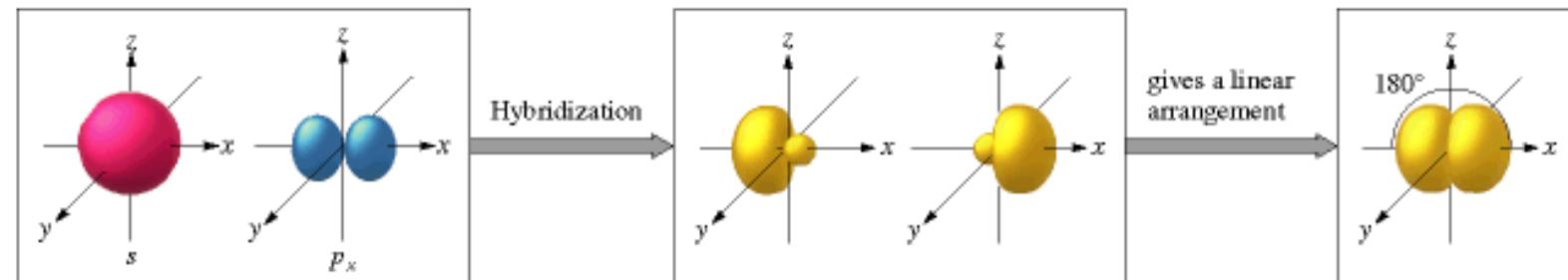


# Hybridization

- Carbon hybridization:
  - $sp$  hybridization → linear combination of a  $s$  and a  $p$  orbital.



Acetylene, a linear molecule with a triple C-C bond.



# Electronic structure of conjugated molecules



# Electronic structure of conjugated molecules

- Conjugated molecules:

- Those with connected  $p$  orbitals with delocalized electrons, which in general lowers the overall energy of the molecule and increases stability -> **alternating multiple/single bond.**



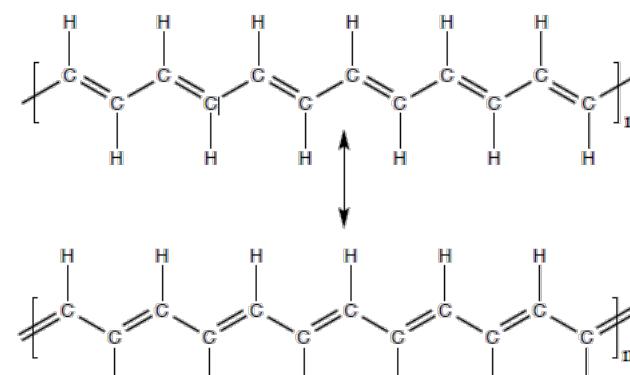
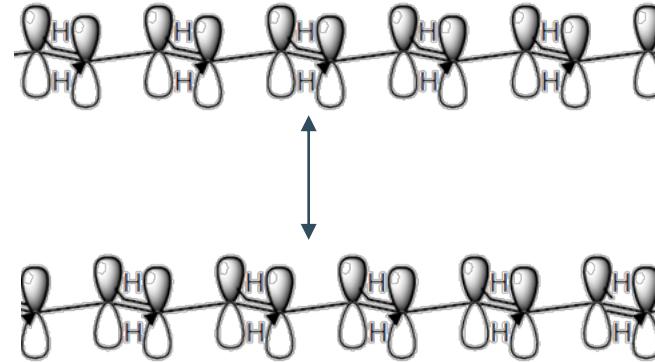
- In most polyatomic molecules, bonding can be described in terms of MOs that are essentially localized on individual bonds (built from AOs of two neighboring atoms). This approach breaks down for conjugated compounds.

# Electronic structure of conjugated molecules

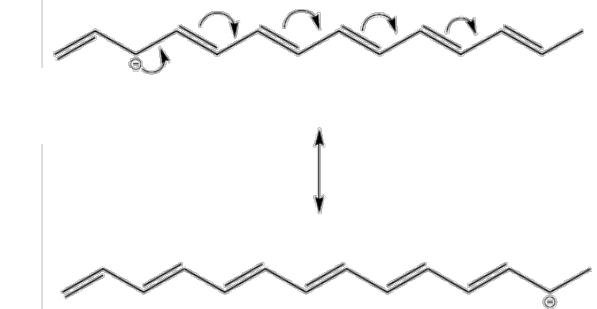
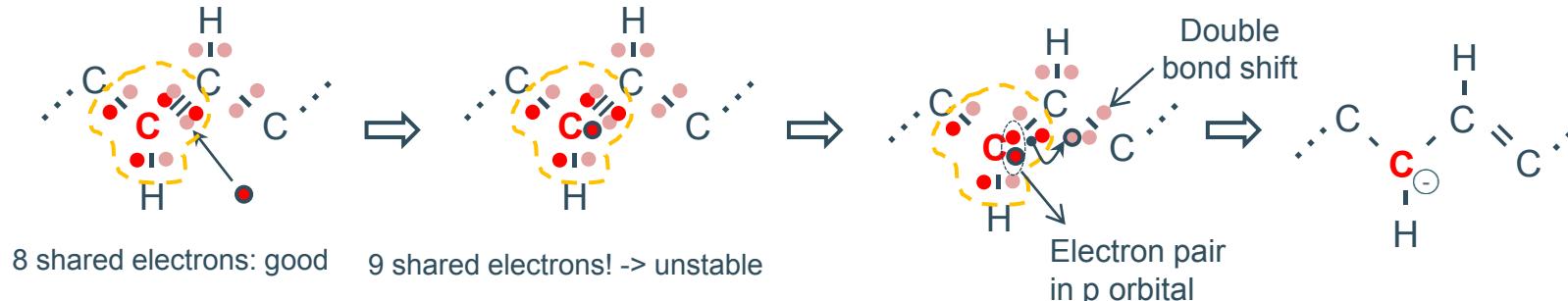
- Conjugated molecules: delocalization

- $\pi$ - bonding between  $sp^2$  C atoms results in delocalized MOs.

Two resonance structures  
(polyacetylene):



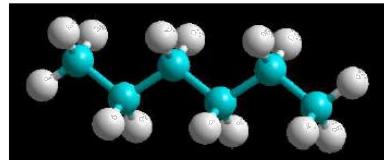
- Charges can be delocalized due to resonance structures -> Charge transport in plastics!!



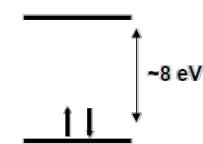
# Electronic structure of conjugated molecules

- Conjugated molecules: delocalization
  - Orbitals extend to the whole molecule

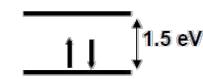
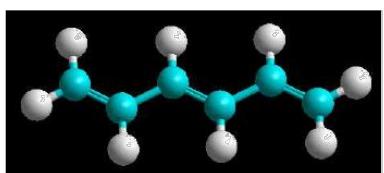
Polyethylene: insulator



Energy Gap



Polyacetylene: semiconductor



- Nobel Prize in chemistry 2000 "for the discovery and development of conductive polymers"

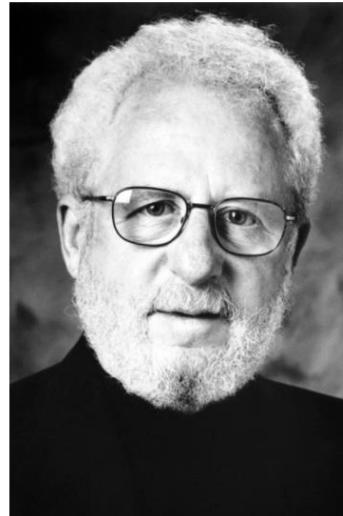


Photo from the Nobel Foundation archive.

Alan J. Heeger

Prize share: 1/3

UC Santa Barbara



Photo from the Nobel Foundation archive.

Alan G. MacDiarmid

Prize share: 1/3

University of Pennsylvania



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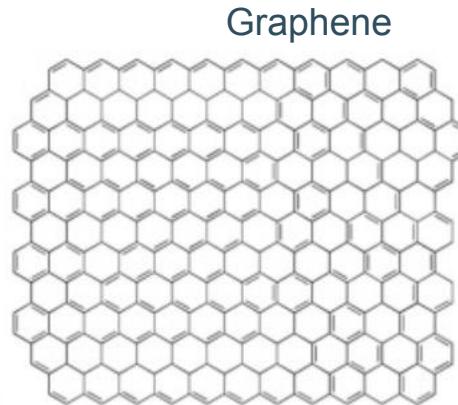
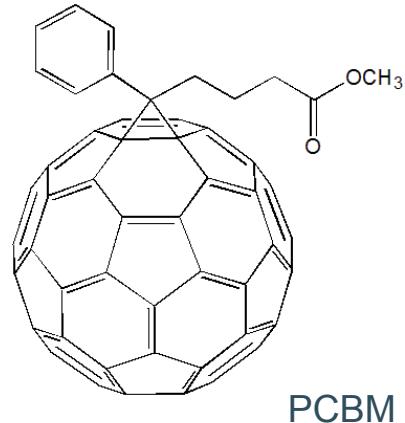
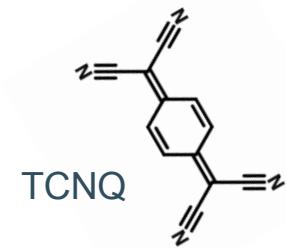
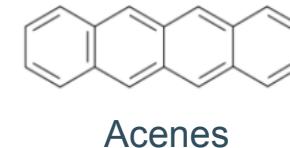
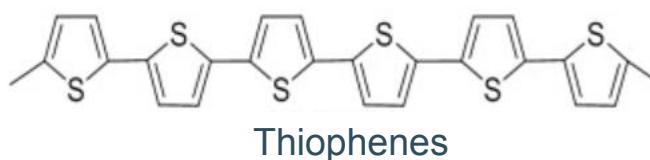
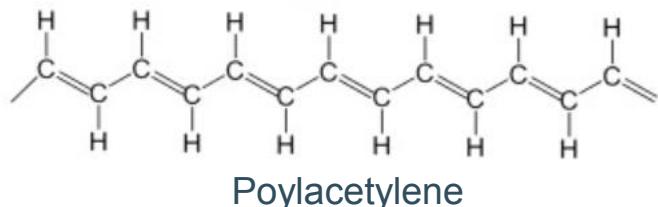
Hideki Shirakawa

Prize share: 1/3

University of Tsukuba

# Electronic structure of conjugated molecules

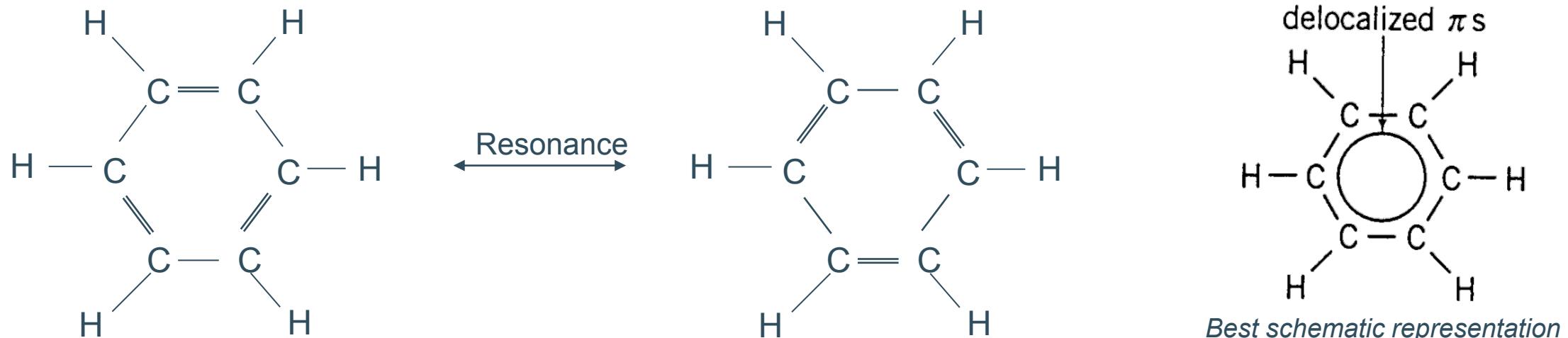
- Conjugated molecules: examples



# Electronic structure of conjugated molecules

- Conjugated molecules: Benzene

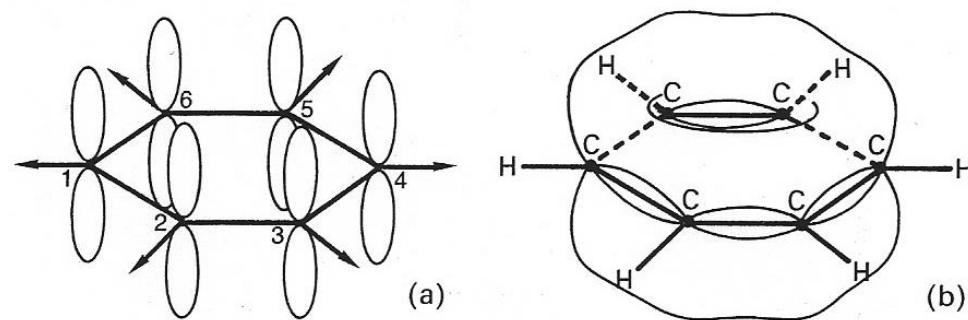
- Each of the C atoms are in a  $sp^2$  hybridized state, forming a  $\sigma$  bond with H, a single  $\sigma$  bond with one neighbor C atom, and a double ( $\sigma$  and  $\pi$ ) bond with its other C neighbor. The  $\pi$  bonds results from the overlap between two adjacent  $2p_z$  orbitals, considering the molecule lies in the (x, y) plane (planar molecule).



Benzene rings are often drawn with alternating single and double bonds. However, experiments make it clear that **all C-C bonds in benzene are equivalent**, and the strengths and lengths of the C-C bonds are intermediate between single and double bonds.

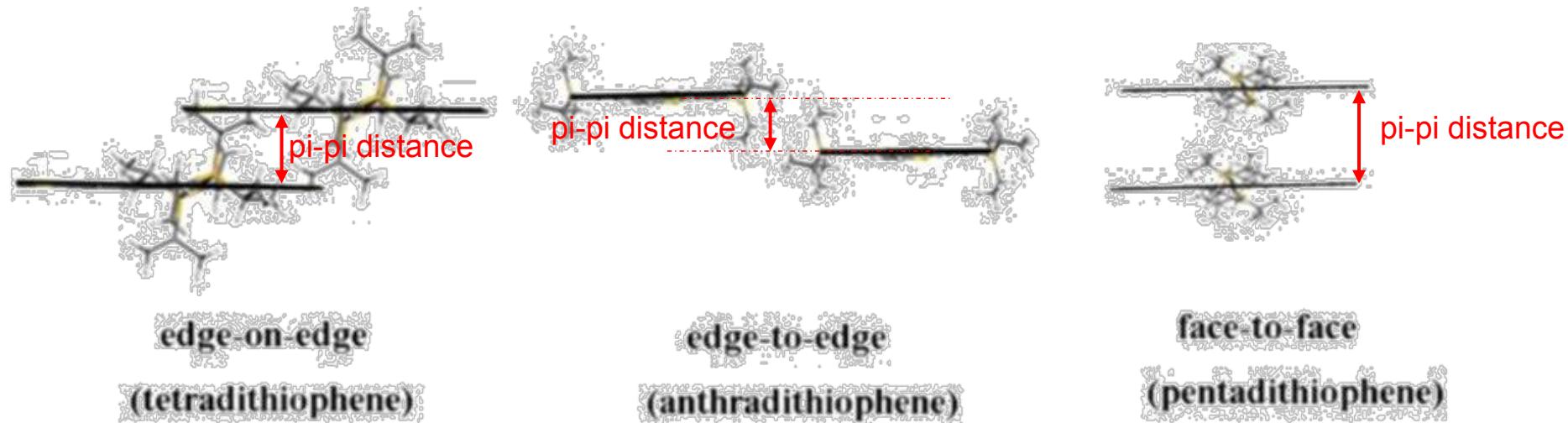
# Electronic structure of conjugated molecules

- Conjugated molecules: Benzene
  - The  $\pi$  bonds results from the overlap between two adjacent  $2p_z$  orbitals, considering the molecule lies in the  $(x, y)$  plane.



# Electronic structure of conjugated molecules

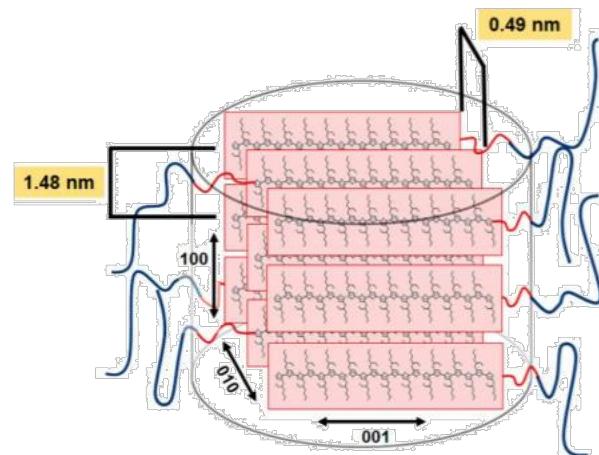
- Conjugated molecules:  $\pi$ - $\pi$  stacking
  - Noncovalent interactions between aromatic rings.



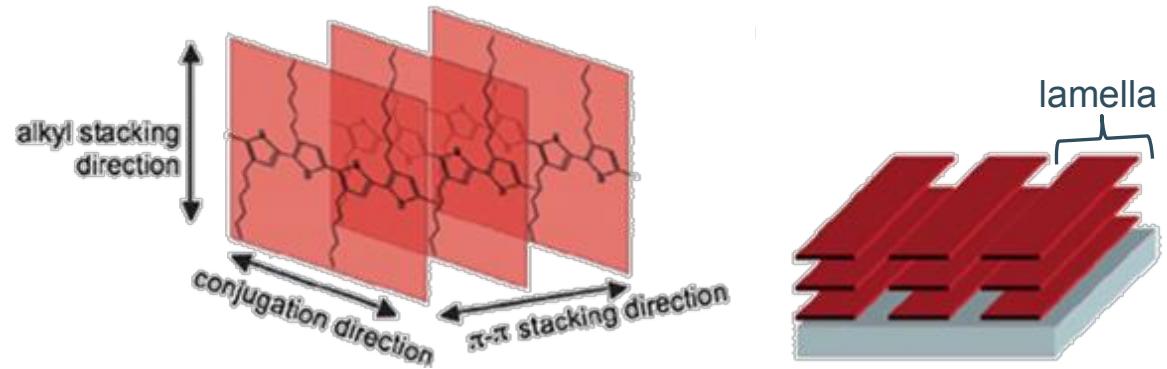
Configurations of three typical lamellar  $\pi$ - $\pi$  stacking  
(Journal of Materials Science 53(46), DOI: 10.1007/s10853-018-2719-0)

# Electronic structure of conjugated molecules

- Conjugated molecules:  $\pi$ - $\pi$  stacking
  - Responsible of the lamella formation in electronic polymers.
  - Leads to the crystallinity of electronic polymers. Electronic polymers are semicrystalline (amorphous and crystalline domains coexist).
  - Conduction is best intramolecular (along conjugation direction) and along pi-pi stacking direction.



(Macromolecules 2017, 50, 6128–6136, DOI: 10.1021/acs.macromol.7b01323)

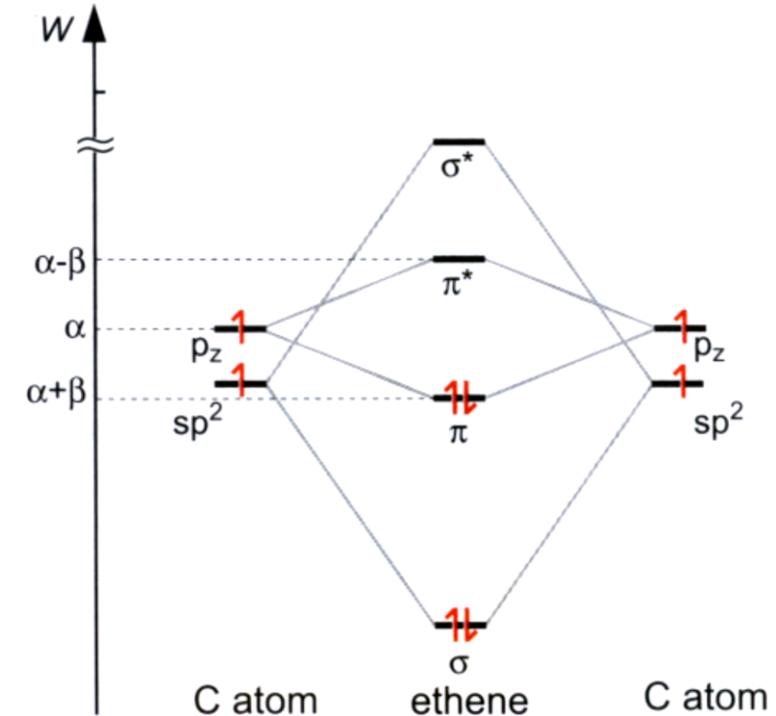


Formation of polymer lamella  
(Polym. Chem., 2013, 4, 5197-5205, <https://doi.org/10.1039/C3PY00131H>)

# Electronic structure of conjugated molecules

- Conjugated molecules: Energy structure
  - The delocalization of the  $\pi$  electrons gives rises to a stable and strong bonding between the C atoms.
  - When considering the electronic properties of conjugated systems, one need only to consider the delocalized  $\pi$  electrons (treated as valence electrons), usually lying at a higher energy level rather than the  $\sigma$  electrons (treated as core electrons).

Schematic energy diagram typical of a C=C bond



# Electronic structure of conjugated molecules

- Conjugated molecules: Energy structure. The Hückel method.
  - Applying the LCAO method to conjugated planar systems (called Hückel method when applied to  $\pi$  electrons) allows to understand their electronic properties. We can illustrate this with benzene. With LCAO-MO theory, we can understand the benzene molecule by constructing delocalized  $\pi$  MOs that extend around the entire molecule:  $\psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4 + c_5\phi_5 + c_6\phi_6$
  - Each of the  $\phi_i$  are  $2p$  AOs, centered on each of the six carbon atoms and directed out of the molecular plane. The ring nature of benzene requires that  $\phi_6$  bonds with  $\phi_1$ , as well as with  $\phi_5$ .
  - In the Hückel approximation the following simplifying assumptions are made:
    1. The Coulomb integrals  $H_{ii}$  for each  $\phi_i$  are all the same (call them  $\alpha$ ).
    2. The bond integrals  $H_{jj}$  for each  $\phi_i$  from adjacent carbon atoms are all the same (call them  $\beta < 0$ ) and the bond integrals from nonadjacent AOs are all zero.  $\beta$  is also called the transfer integral.
    3. The overlap integrals  $S_{ij} = \int \phi_i \phi_j dV$  are all zero. This assumption can be made legitimate with modest adjustments in the AOs. It is a severe approximation that makes the physics less realistic but the maths easier.

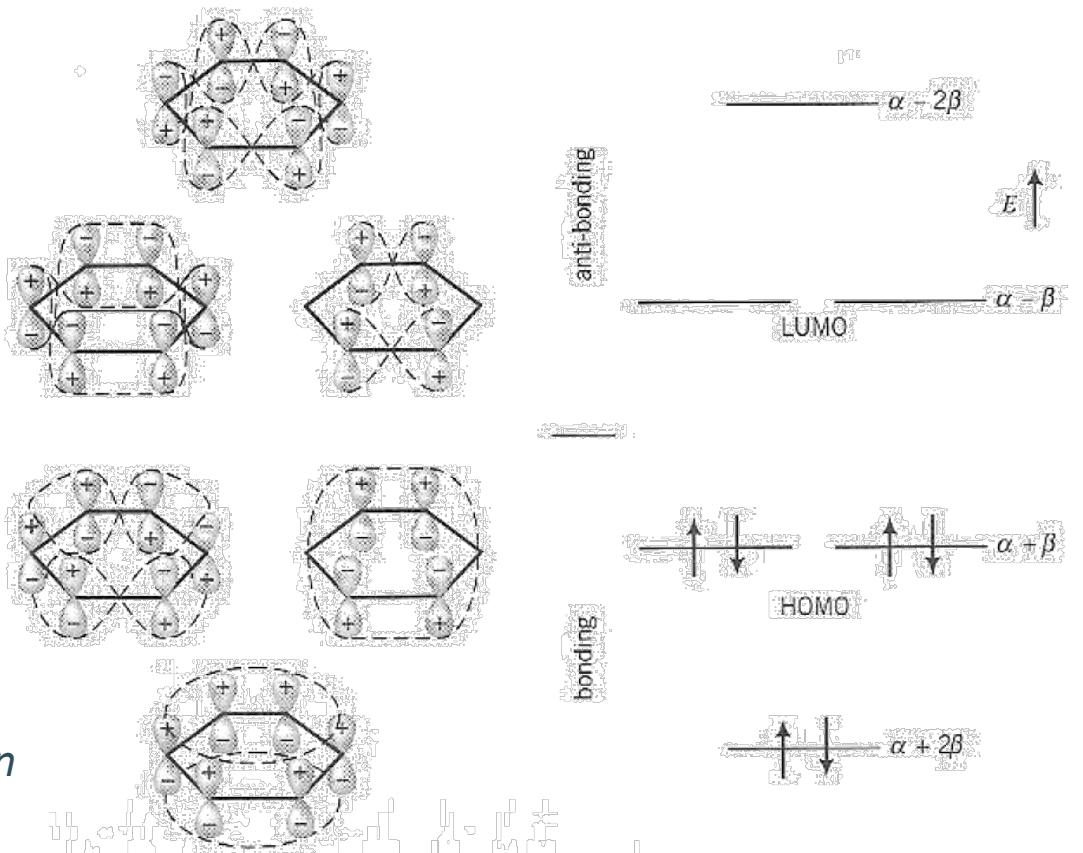
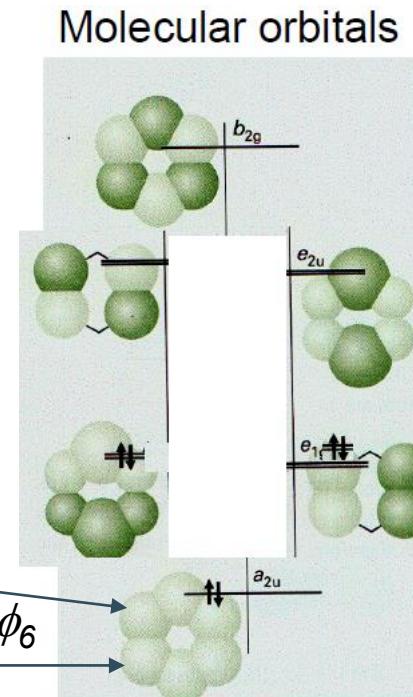
# Electronic structure of conjugated molecules

- Conjugated molecules: Energy structure. The Hückel method.

- Applying the Hückel method to benzene results in the electronic structure schematically illustrated below.

$$\psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4 + c_5\phi_5 + c_6\phi_6$$

Schematic MOs and energy levels for delocalized  $\pi$  electrons in benzene molecule from Hückel model.



# Electronic structure of conjugated molecules

- Conjugated molecules: Energy structure. The Hückel method.
  - Applying the Hückel method to benzene...

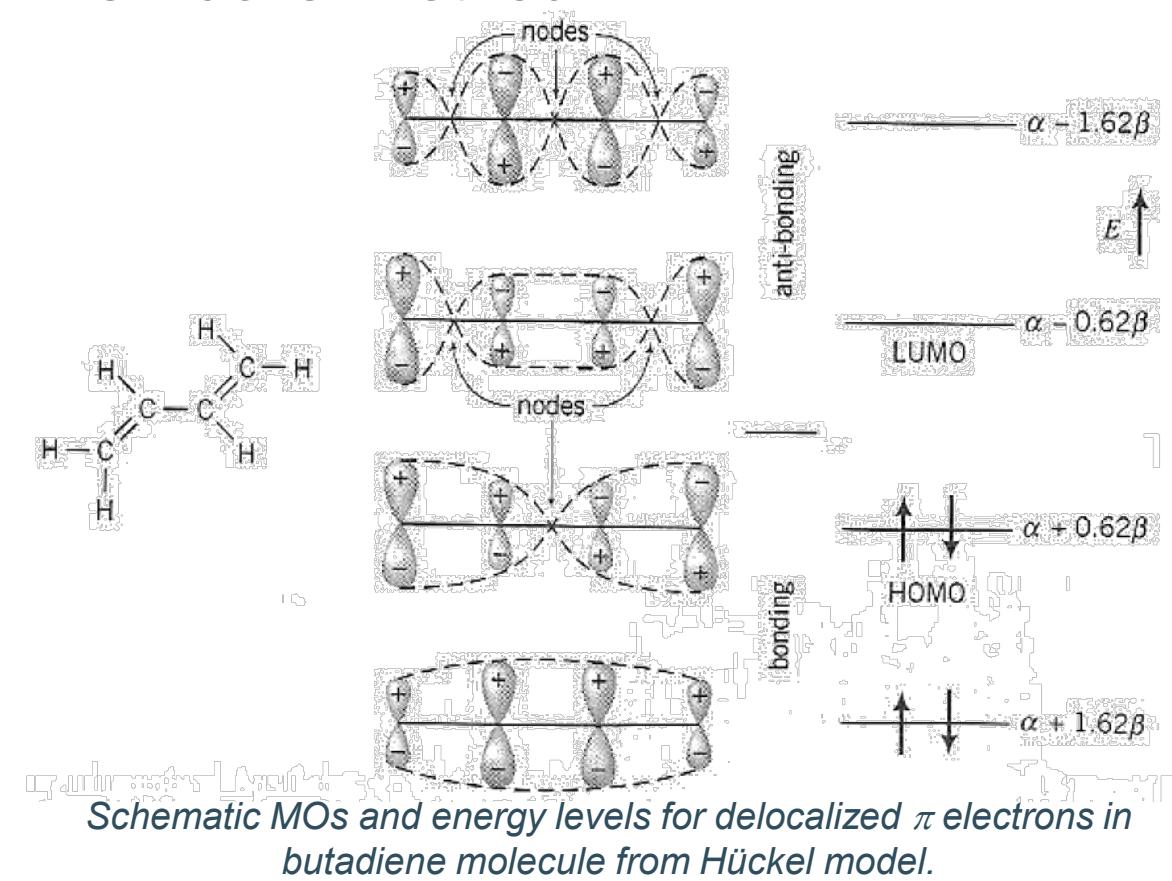
1. Yields 6 MOs (three bonding and three antibonding). The lowest energy MO corresponds to all  $c_i$  being equal. The highest energy MO corresponds to  $c_i$  with alternating signs, with nodal planes between each atom pair.
2. Also shown are the corresponding energy levels, which include two pairs of degenerate levels. The energy of the bottom level is found to be  $\alpha + 2\beta$  (the bond integral  $\beta$  is negative).
3. There are two degenerate bonding MOs with  $E = \alpha + \beta$  (these are the Highest Occupied MOs, the '**HOMO**' levels), two degenerate antibonding MOs with  $E = \alpha - \beta$  (these are the Lowest Unoccupied MOs, the '**LUMO**' levels), and the highest antibonding MO level with  $E = \alpha - 2\beta$ .
4. The Coulomb energy  $\alpha$  represents the reference state for the  $2p$  electrons, and the difference in energy between the highest and lowest level is four times the bond integral  $\beta$ .
5. In the ground state of the benzene molecule, the three bonding levels are occupied, and the three antibonding levels are unoccupied.

# Electronic structure of conjugated molecules

- Conjugated molecules: Energy structure. The Hückel method.
  - Applying the Hückel method to butadiene...

\*Notice that the amplitude of the molecular MO is modulated by a sinusoid with wavelength ( $\lambda$ )

->Higher energy bands have more nodes which means larger values of the wavenumber  $k = 2\pi/\lambda$



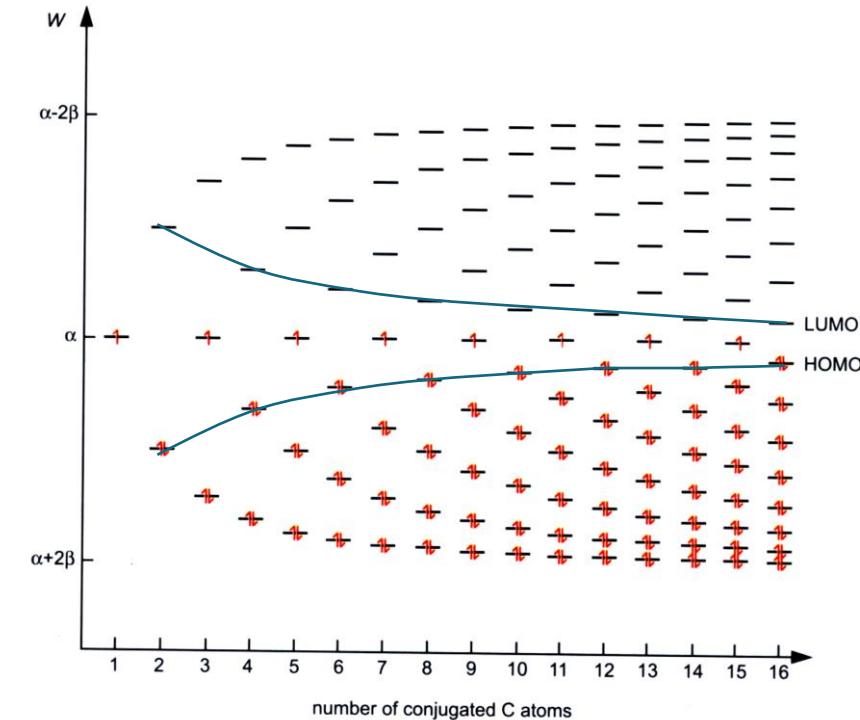
# Electronic structure of conjugated molecules

- Conjugated molecules: Energy structure. The Hückel method.
    - Applying the Hückel method to butadiene...
1. Each of the carbon atoms in butadiene ( $C_4H_6$ ) has three neighbors and  $sp^2$  hybrids form  $\sigma$  bonds. The remaining  $2p$  AOs, directed out of the molecular plane, form delocalized  $\pi$  MOs that extend along the carbon chain, and can be treated in the Hückel approximation.
  2. The figure shows the relative orientation of the  $p$  AOs in each of the four MOs (two bonding, two antibonding), with dashed lines suggesting the outline of the various MOs. The four energy levels are  $\alpha + 1.62\beta$ ,  $\alpha + 0.62\beta$ ,  $\alpha - 0.62\beta$ , and  $\alpha - 1.62\beta$ .

# Electronic structure of conjugated molecules

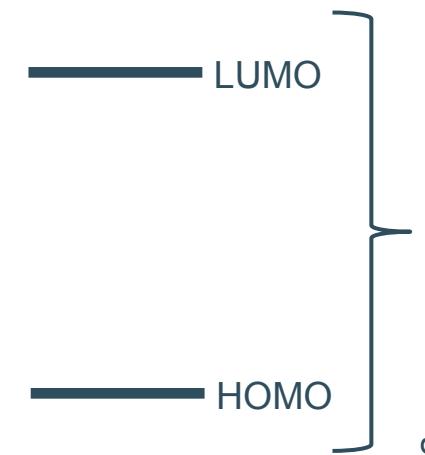
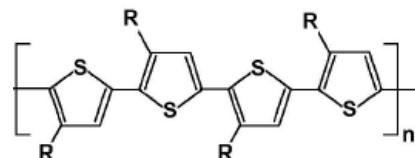
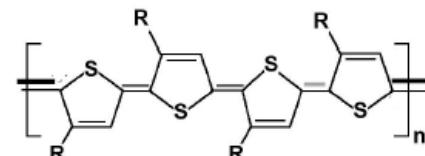
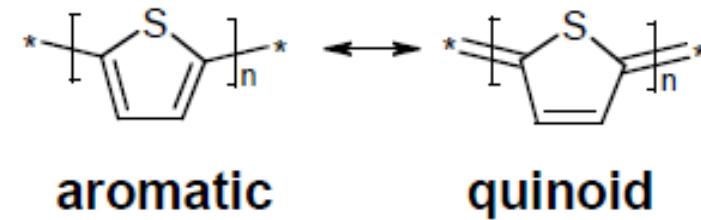
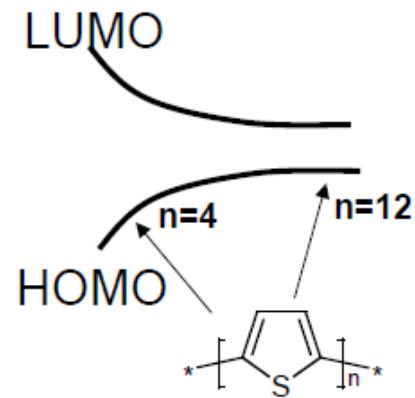
- Conjugated molecules: Energy structure. HOMO and LUMO shifting.
  - The highest occupied orbital (HOMO) corresponds to the valence band edge of a semiconductor, while the lowest unoccupied orbital (LUMO) corresponds to the conduction band edge. The band-gap thus corresponds to the difference between HOMO and LUMO energy levels.
  - All the levels are confined in between an energy interval of  $4\beta$ .

*Energy levels and electron occupation for conjugated hydrocarbon with unbranched chain structures of one to 16 C atoms as calculated by the HMO theory. The system with one C atom represents a  $sp^2$  hybridized  $CH_3$  radical.*



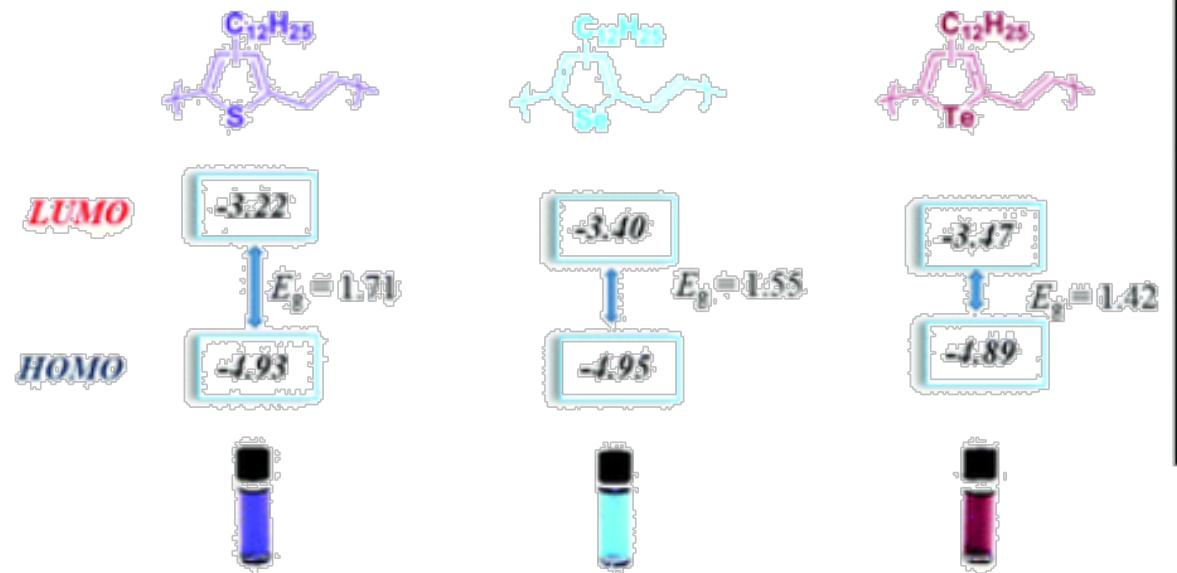
# Electronic structure of conjugated molecules

- Conjugated molecules: Energy structure. HOMO and LUMO shifting.
  - Example for polythiophene.



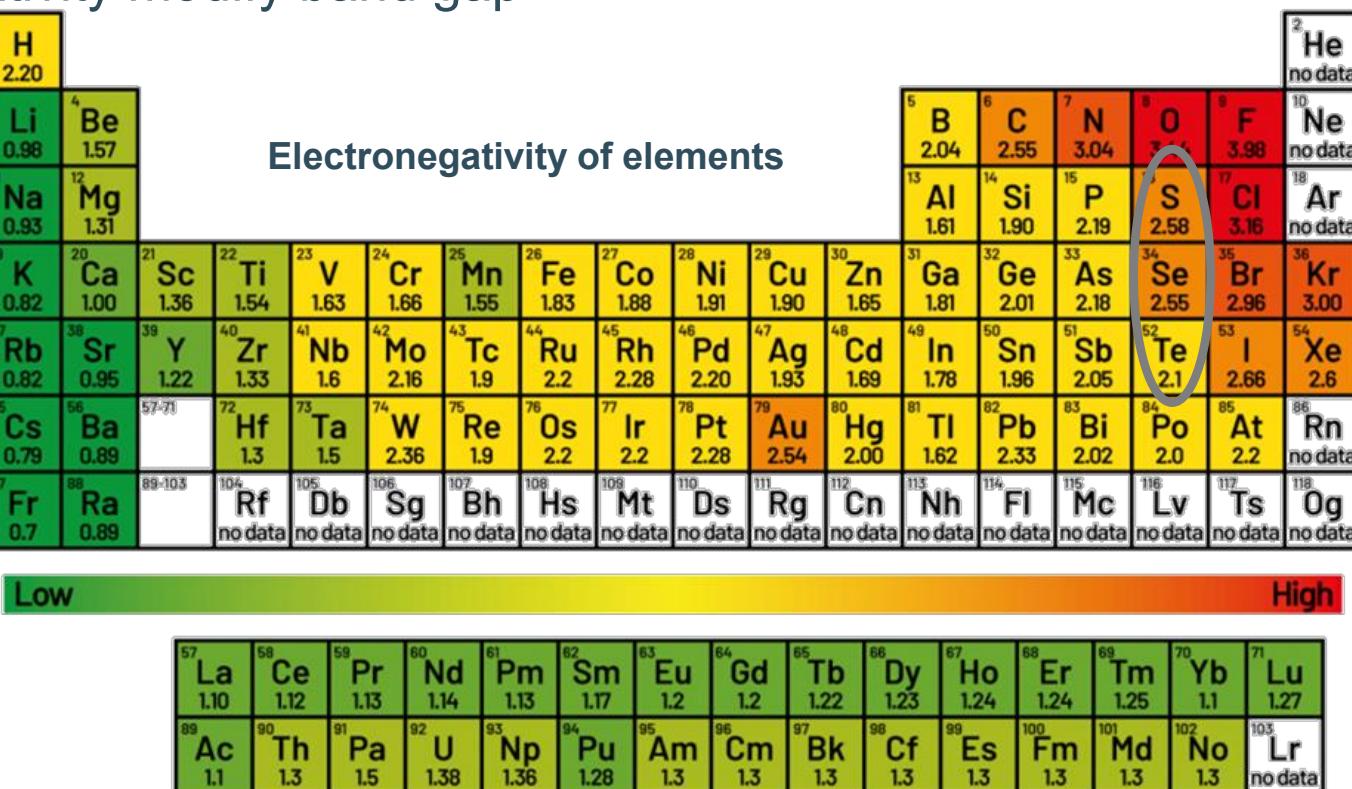
# Electronic structure of conjugated molecules

- Conjugated molecules: Energy structure. HOMO and LUMO shifting.
  - Heteroatoms with different electronegativity modify band gap



|  |
|--|
| <sup>1</sup> H<br>2.20                 |
| <sup>3</sup> Li<br>0.98                |
| <sup>4</sup> Be<br>1.57                |
| <sup>11</sup> Na<br>0.93               |
| <sup>12</sup> Mg<br>1.31               |
| <sup>19</sup> K<br>0.82                |
| <sup>20</sup> Ca<br>1.00               |
| <sup>21</sup> Sc<br>1.36               |
| <sup>22</sup> Ti<br>1.54               |
| <sup>23</sup> V<br>1.63                |
| <sup>24</sup> Cr<br>1.66               |
| <sup>25</sup> Mn<br>1.55               |
| <sup>26</sup> Fe<br>1.83               |
| <sup>27</sup> Co<br>1.88               |
| <sup>28</sup> Ni<br>1.91               |
| <sup>29</sup> Cu<br>1.90               |
| <sup>30</sup> Zn<br>1.65               |
| <sup>31</sup> Ga<br>1.81               |
| <sup>32</sup> Ge<br>2.01               |
| <sup>33</sup> As<br>2.18               |
| <sup>34</sup> Se<br>2.55               |
| <sup>35</sup> Br<br>2.96               |
| <sup>36</sup> Kr<br>3.00               |
| <sup>5</sup> B<br>2.04                 |
| <sup>6</sup> C<br>2.55                 |
| <sup>7</sup> N<br>3.04                 |
| <sup>8</sup> O<br>3.44                 |
| <sup>9</sup> F<br>3.98                 |
| <sup>10</sup> Ne<br>no data            |
| <sup>13</sup> Al<br>1.61               |
| <sup>14</sup> Si<br>1.90               |
| <sup>15</sup> P<br>2.19                |
| <sup>17</sup> Cl<br>3.16               |
| <sup>18</sup> Ar<br>no data            |
| <sup>37</sup> Rb<br>0.82               |
| <sup>38</sup> Sr<br>0.95               |
| <sup>39</sup> Y<br>1.22                |
| <sup>40</sup> Zr<br>1.33               |
| <sup>41</sup> Nb<br>1.6                |
| <sup>42</sup> Mo<br>2.16               |
| <sup>43</sup> Tc<br>1.9                |
| <sup>44</sup> Ru<br>2.2                |
| <sup>45</sup> Rh<br>2.28               |
| <sup>46</sup> Pd<br>2.20               |
| <sup>47</sup> Ag<br>1.93               |
| <sup>48</sup> Cd<br>1.69               |
| <sup>49</sup> In<br>1.78               |
| <sup>50</sup> Sn<br>1.96               |
| <sup>51</sup> Sb<br>2.05               |
| <sup>52</sup> Te<br>2.1                |
| <sup>53</sup> I<br>2.66                |
| <sup>54</sup> Xe<br>2.6                |
| <sup>55</sup> Cs<br>0.79               |
| <sup>56</sup> Ba<br>0.89               |
| <sup>57</sup> - <sup>71</sup> no data  |
| <sup>72</sup> Hf<br>1.3                |
| <sup>73</sup> Ta<br>1.5                |
| <sup>74</sup> W<br>2.36                |
| <sup>75</sup> Re<br>1.9                |
| <sup>76</sup> Os<br>2.2                |
| <sup>77</sup> Ir<br>2.2                |
| <sup>78</sup> Pt<br>2.28               |
| <sup>79</sup> Au<br>2.54               |
| <sup>80</sup> Hg<br>2.00               |
| <sup>81</sup> Tl<br>1.62               |
| <sup>82</sup> Pb<br>2.33               |
| <sup>83</sup> Bi<br>2.02               |
| <sup>84</sup> Po<br>2.0                |
| <sup>85</sup> At<br>2.2                |
| <sup>86</sup> Rn<br>no data            |
| <sup>87</sup> Fr<br>0.7                |
| <sup>88</sup> Ra<br>0.89               |
| <sup>89</sup> - <sup>103</sup> no data |
| <sup>104</sup> Rf<br>no data           |
| <sup>105</sup> Db<br>no data           |
| <sup>106</sup> Sg<br>no data           |
| <sup>107</sup> Bh<br>no data           |
| <sup>108</sup> Hs<br>no data           |
| <sup>109</sup> Mt<br>no data           |
| <sup>110</sup> Ds<br>no data           |
| <sup>111</sup> Rg<br>no data           |
| <sup>112</sup> Cn<br>no data           |
| <sup>113</sup> Nh<br>no data           |
| <sup>114</sup> Fl<br>no data           |
| <sup>115</sup> Mc<br>no data           |
| <sup>116</sup> Lv<br>no data           |
| <sup>117</sup> Ts<br>no data           |
| <sup>118</sup> Og<br>no data           |

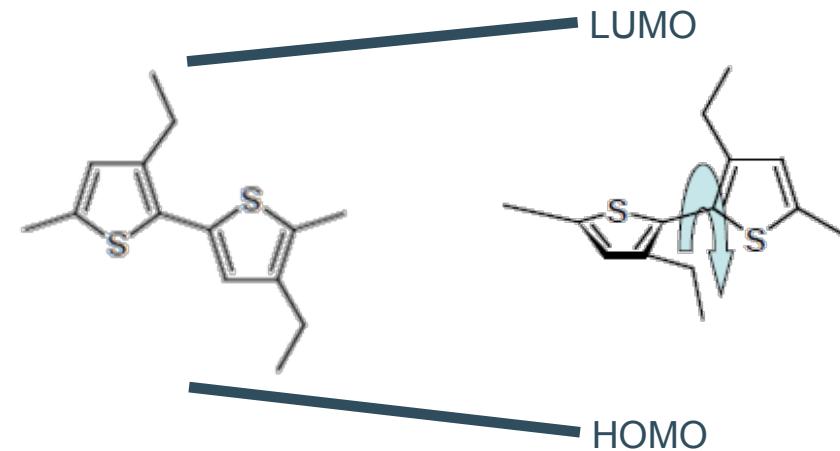
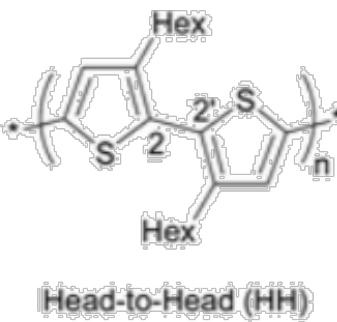
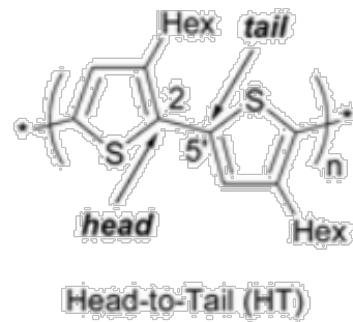
Electronegativity of elements



<https://doi.org/10.1039/C5SC03501E>

# Electronic structure of conjugated molecules

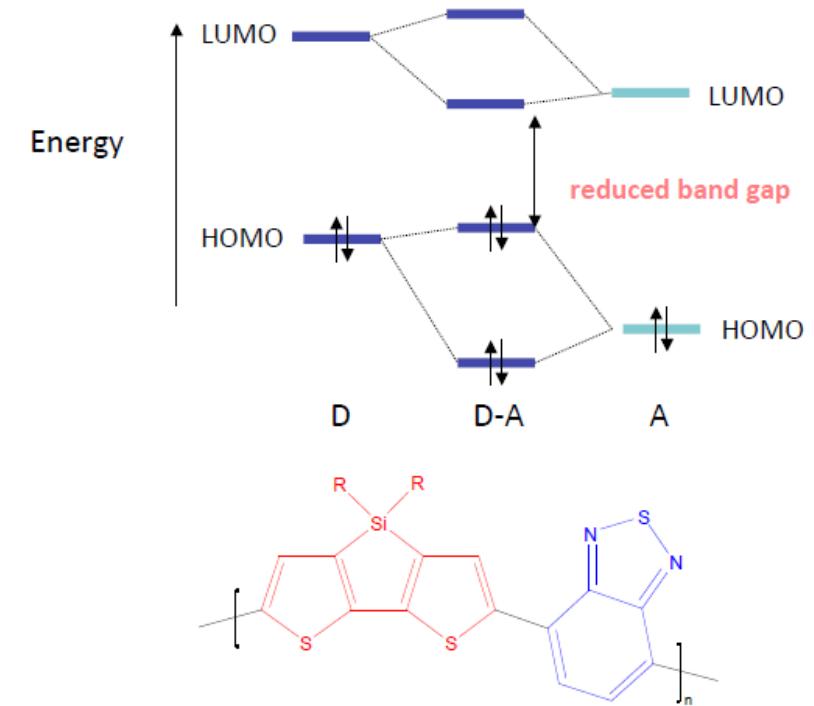
- Conjugated molecules: Energy structure. HOMO and LUMO shifting
  - Backbone twist



Twist reduce pi-orbital overlap -> bandgap increases

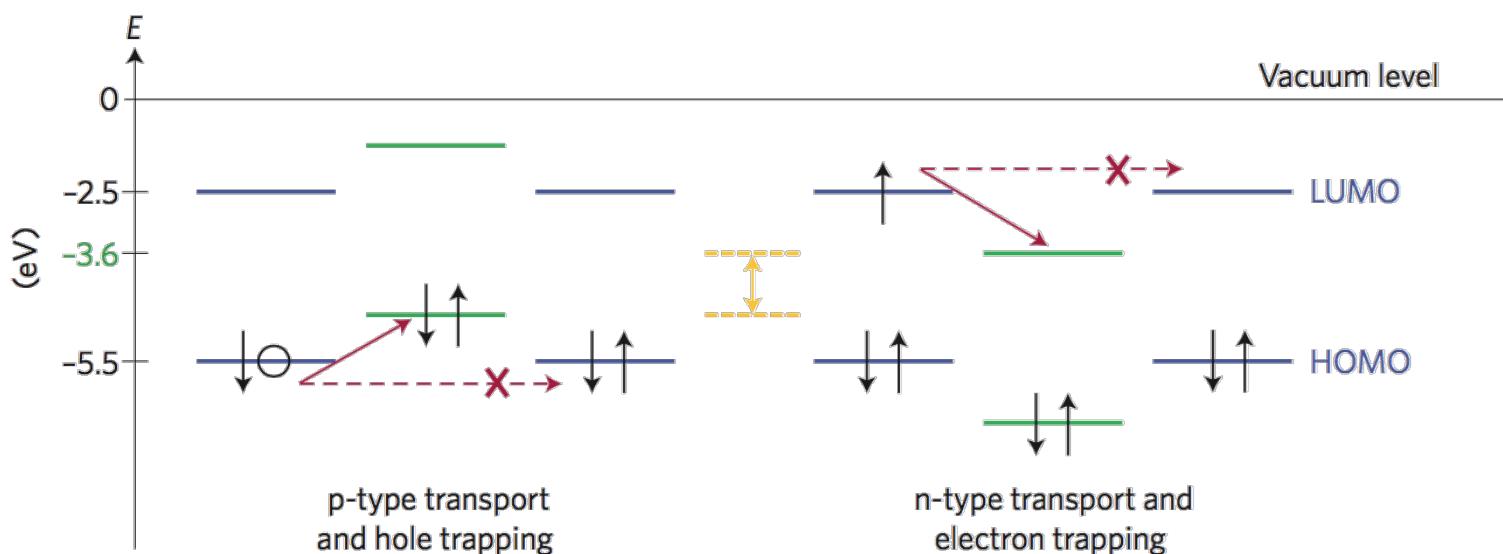
# Electronic structure of conjugated molecules

- Conjugated molecules: Energy structure. HOMO and LUMO shifting
  - Donor-acceptor polymers. The push-pull approach.
  - Molecular orbital hybridization



# Electronic structure of conjugated molecules

- Conjugated molecules: Energy structure. HOMO and LUMO. Why it matters?
  - Charge trapping: Electrons and holes differ strongly in their sensitivity to trapping at defects or impurities. The different susceptibility of electrons and holes to trapping results from the dissimilar energies of the HOMO and LUMO. For most organic semiconductors, the HOMO is located around  $-5$  to  $-6$  eV versus vacuum, whereas the LUMO ranges from about  $-2$  to  $-3$  eV.

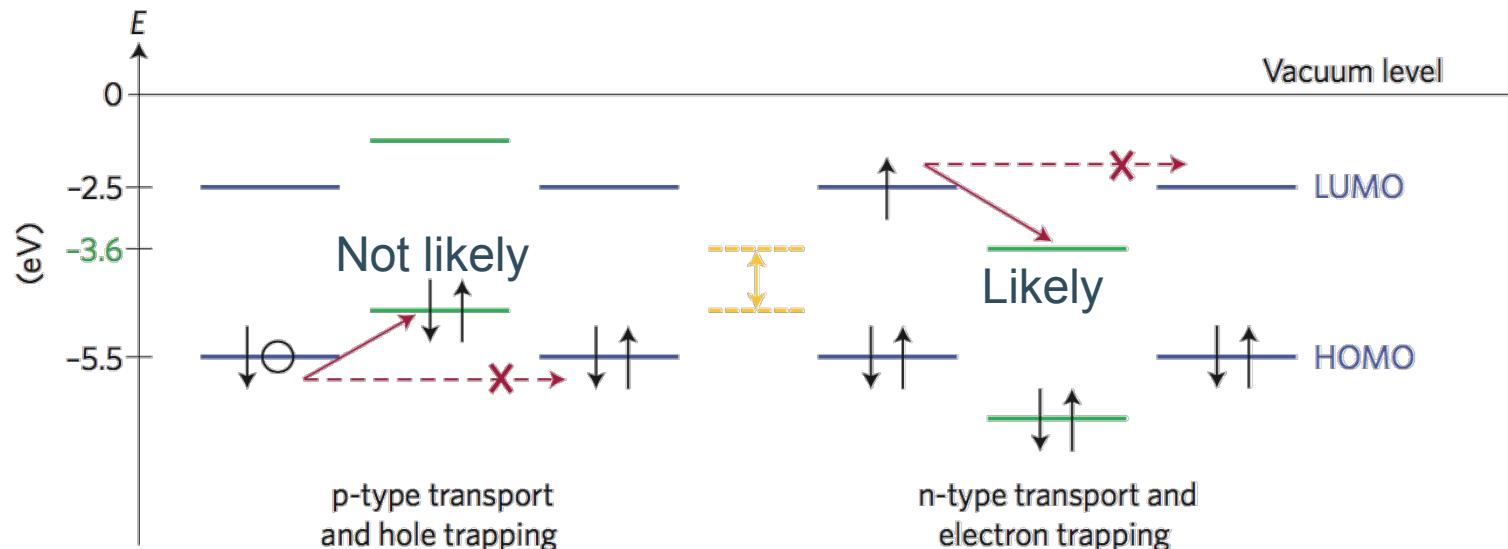


Energy level diagram illustrating hole and electron trapping in organic semiconductor films.

In the case of p-type transport (left), a hole (black circle) can be localized by a higher-lying filled defect level (shown in green) instead of being transferred between the HOMOs of two adjacent molecules (shown in blue). n-type transport (right) requires the transfer of an excess electron (black arrow) between the LUMOs of two molecules (shown in blue). An empty lower-lying defect level (shown in green) can trap the electron for some time until it is released by thermal activation. Trap-free high-mobility transport of both electrons and holes may therefore require materials with a small HOMO–LUMO gap (shown in yellow).

# Electronic structure of conjugated molecules

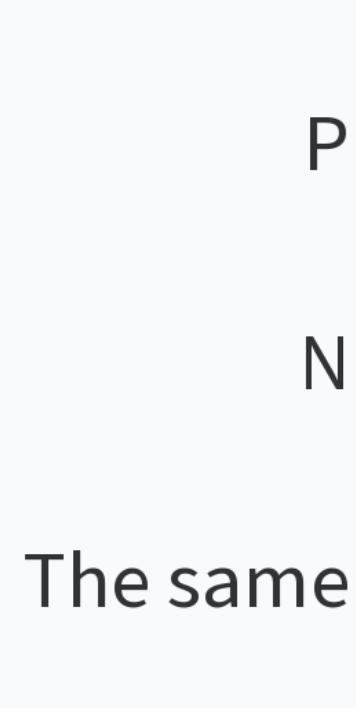
- Conjugated molecules: Energy structure. HOMO and LUMO. Why it matters?
  - Charge trapping: Defects or impurities frequently have empty orbitals between  $-3$  eV and  $-5$  eV that can take up an electron. Filled orbitals above  $-5$  eV (suitable for accepting holes) are more elusive.



*Energy level diagram illustrating hole and electron trapping in organic semiconductor films.*



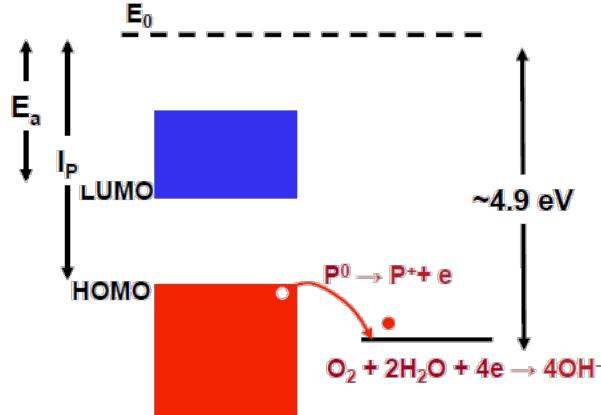
## What kind of material would be more stable: p or n?



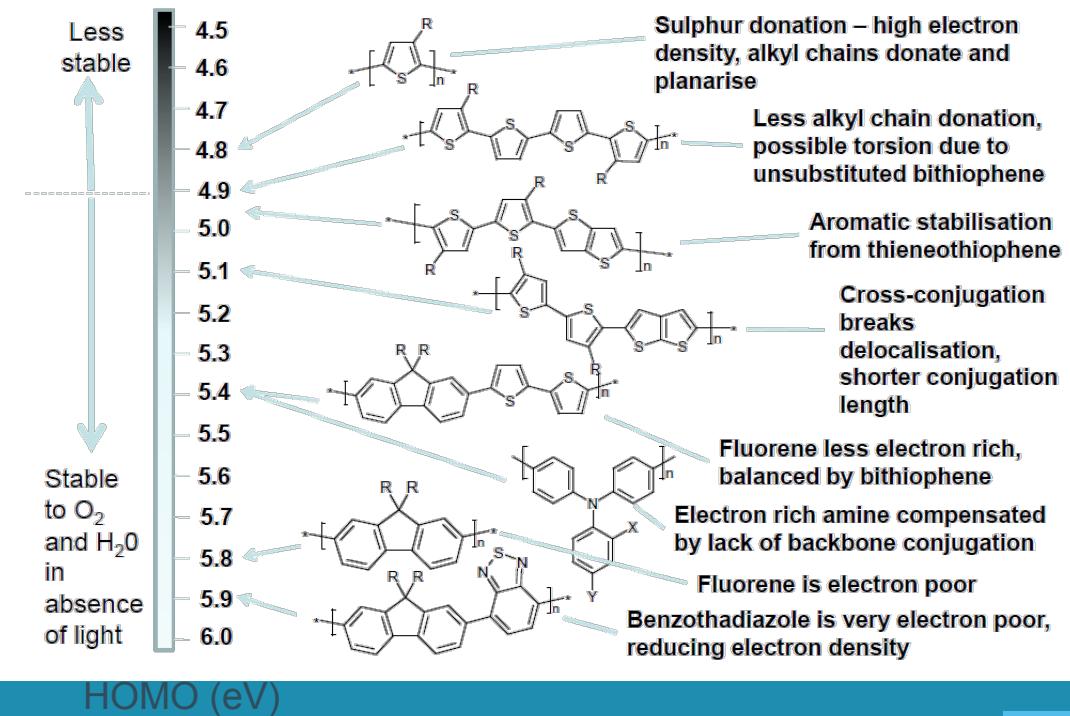
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# Electronic structure of conjugated molecules

- Conjugated molecules: Energy structure. HOMO and LUMO. Why it matters?
  - Ambient stability: Polymers with ionization potential  $I_p < 4.9$  eV get oxidized by wet oxygen. Hence they are unstable in air.
    - In most n-type materials: oxidation traps electrons from the LUMO reducing electron mobility -> **Lack of n-type materials!!**
    - In some p-type materials, oxidation can act as a dopant. P-type materials with low HOMO are more stable. The HOMO can be lowered by making electron poor materials -> Electron withdrawing groups, backbone twist, conjugation break, etc..



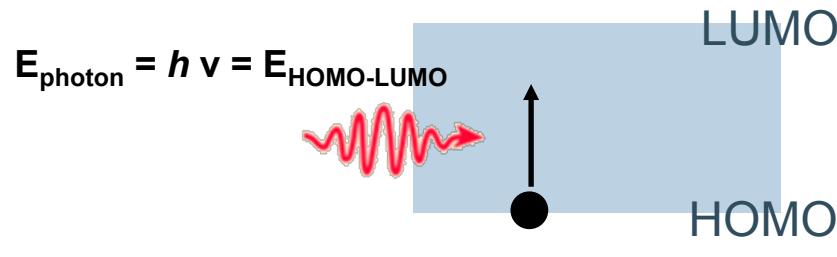
Polymers with  $I_p < 4.9$  eV tend to be unstable with respect to oxidation (=doping) by wet oxygen.



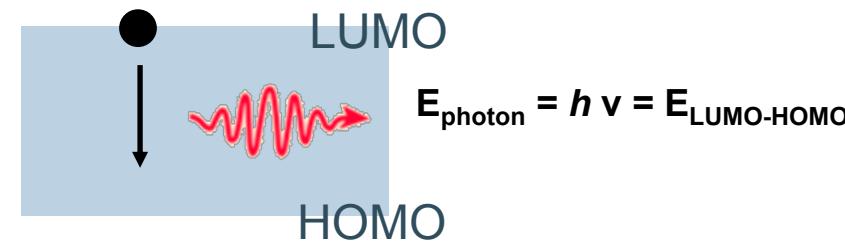
# Electronic structure of conjugated molecules

- Conjugated molecules: Energy structure. HOMO and LUMO. Why it matters?
  - Tuning performance of devices

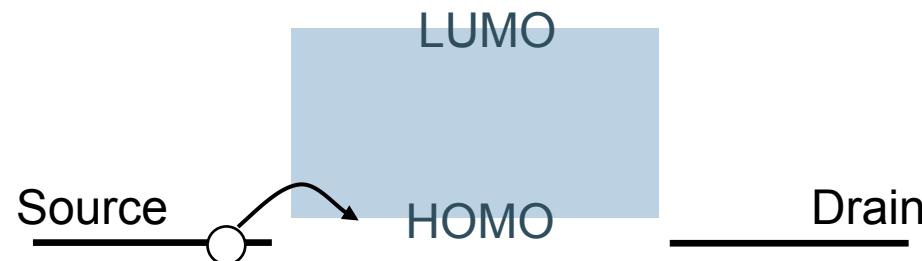
Light absorption:  
Solar cells/photodetectors



Light emission:  
LEDs



Charge injection:  
Transistors



(See Chapter 4)

# Transport in organic electronic materials

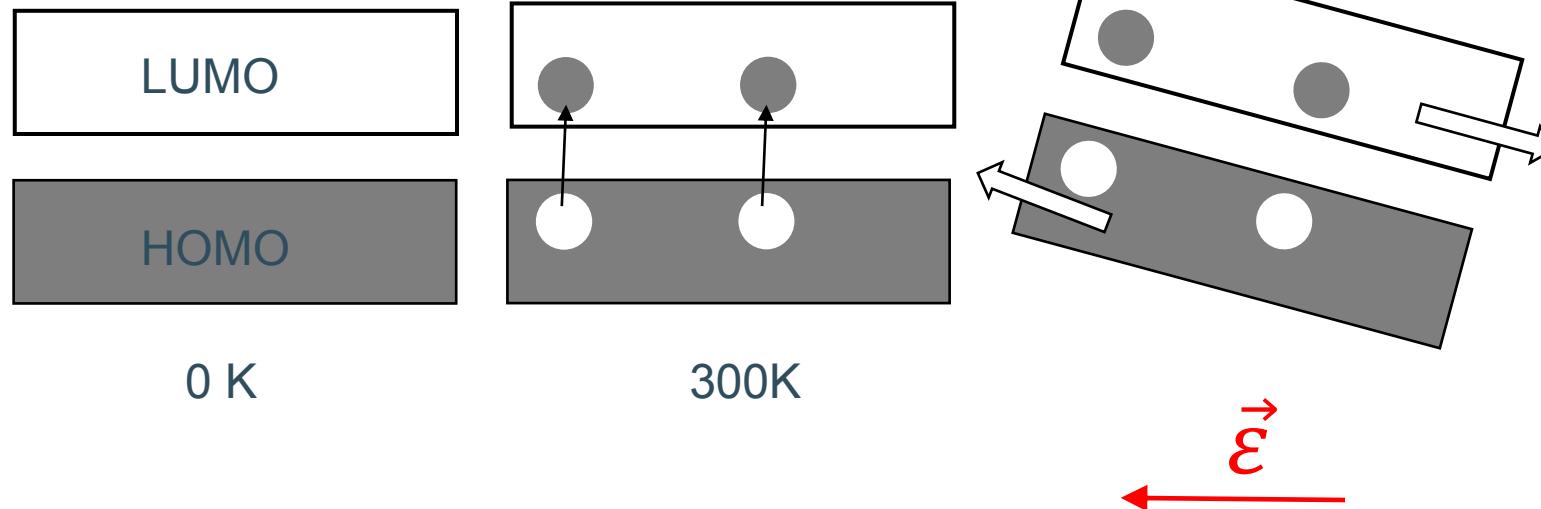
# Transport in organic electronic materials

- Conductivity and mobility

- Current density:  $J = \sigma \epsilon = [n q \mu] \epsilon;$

$$\begin{array}{c} \text{Charge carrier density} \\ \text{Elementary charge} \\ \text{Mobility} \\ \hline \hline \end{array} \quad \begin{array}{c} \text{Conductivity} \\ \text{Electric field} \end{array}$$
$$\mu = \frac{v}{\epsilon}$$

velocity

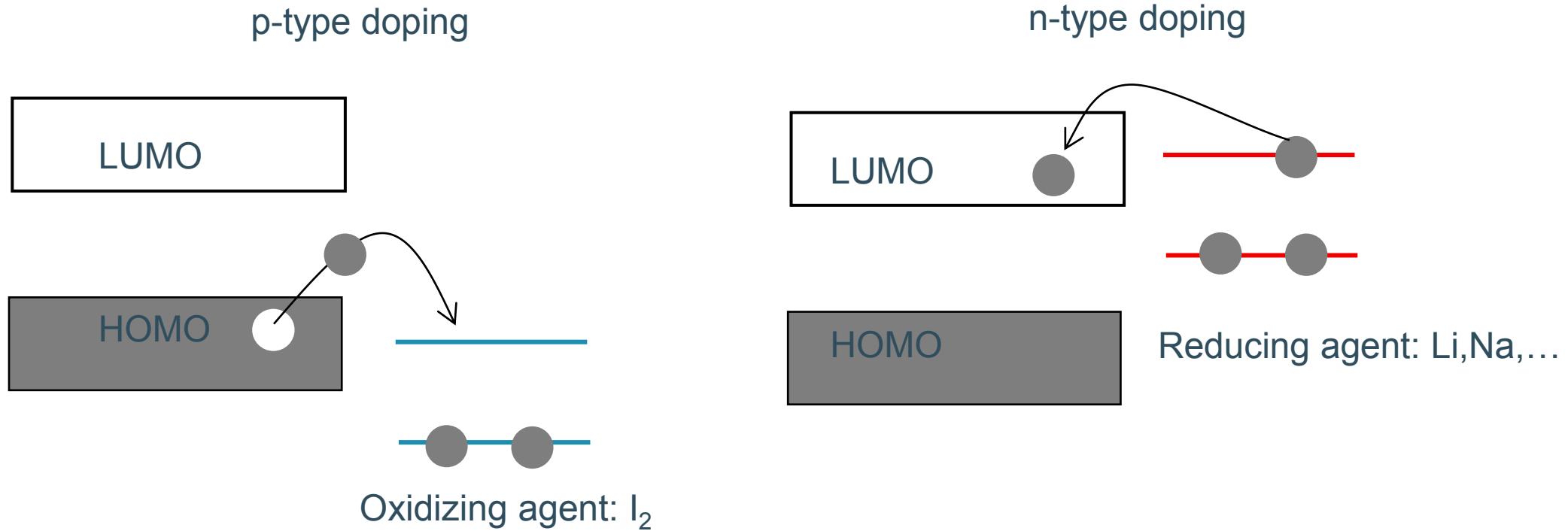


Free charges in OSC induced by:

- Chemical doping
- Photoexcitation
- Injection from electrodes
- Field effect

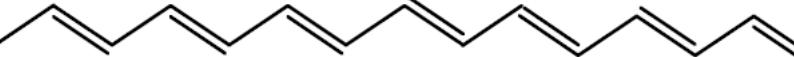
# Transport in organic electronic materials

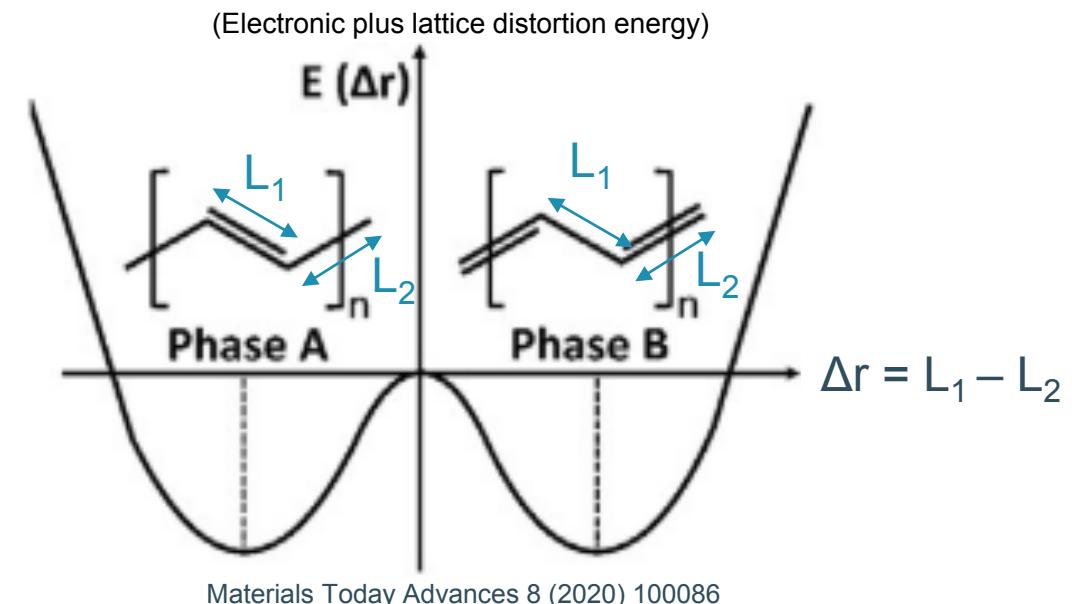
- Doping



# Transport in organic electronic materials

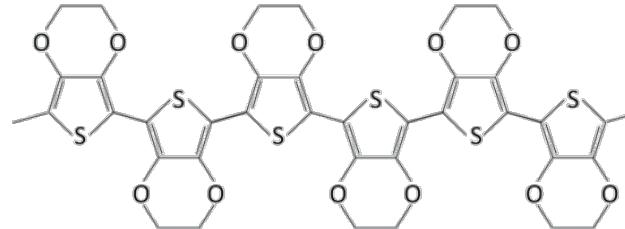
- Degenerated vs non-degenerated conjugated molecules

- In a polymer such as polyacetylene,  the energy of phase A and phase B configurations is the same. The polymer ground state is **degenerate**: all monomers are energetically equivalent with no change in energy of possible alternation of single and double bonds.
- The charge carriers created by doping in degenerated conjugated polymers are called **solitons**.



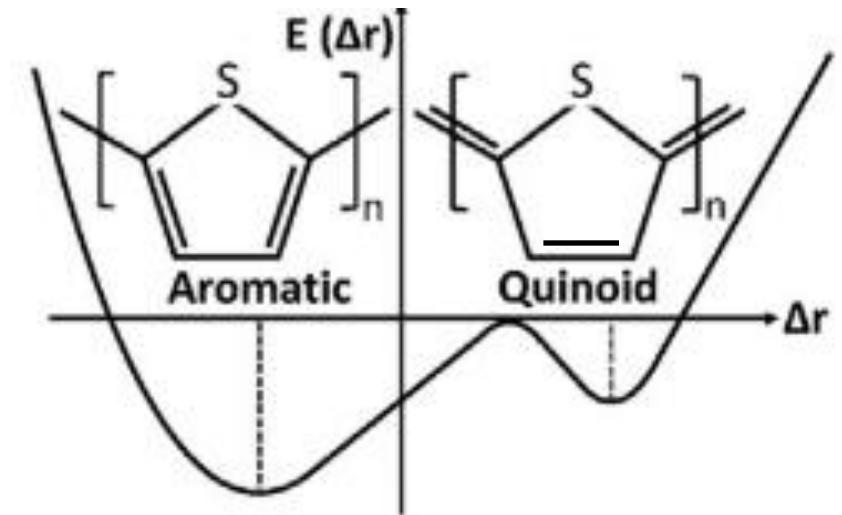
# Transport in organic electronic materials

- Degenerated vs non-degenerated conjugated molecules
  - In a polymer such as PEDOT,



a **non-degenerate** ground-state is present due to the differences in energy between the aromatic (or benzenoid) and quinoid structures.

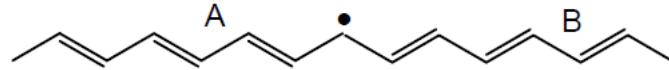
- The charge carriers created by doping in degenerated conjugated polymers are called **polarons and bipolarons**.



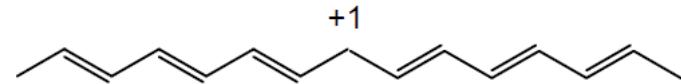
Materials Today Advances 8 (2020) 100086

# Transport in organic electronic materials

- Charges moving in organic semiconductors create changes in the bond-length alternation pattern. Charge transport comes along chain distortion forming quasiparticles.
- Quasi particles: Solitons
  - Solitons: domain boundary between the A and B phases.
  - A soliton can be ionized and transport charge



- A soliton can be ionized and transport charge

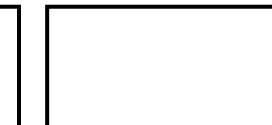


The soliton presents an unpaired  $e^-$  in between HOMO-LUMO (non-bonding level)

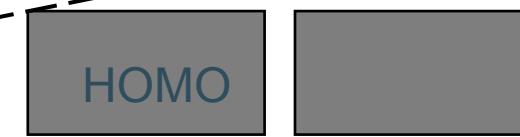
LUMO

HOMO

LUMO

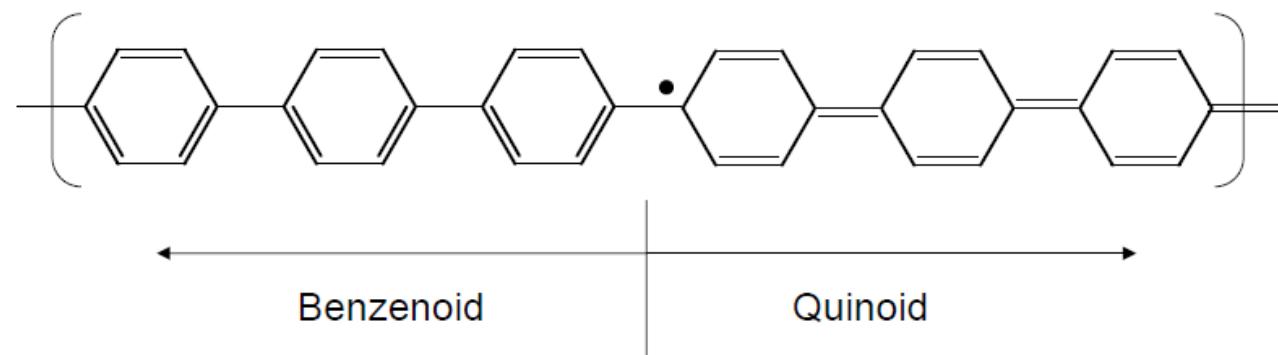


HOMO



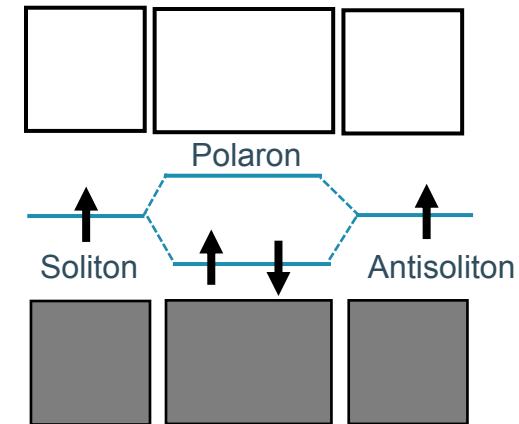
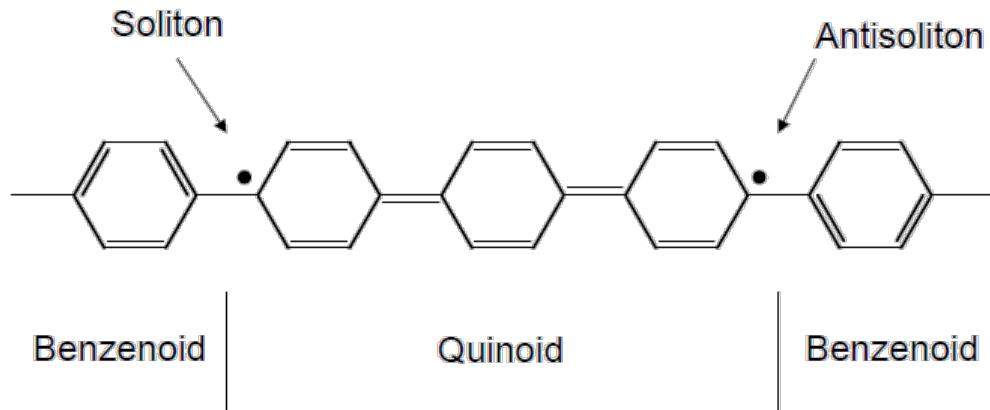
# Transport in organic electronic materials

- Charges moving in organic semiconductors create changes in the bond-length alternation pattern.
- Quasi particles: Solitons
  - Solitons: A soliton in a non-degenerate ground-state conjugated polymer costs energy because the quinoid part has more energy than the benzenoid part. Therefore, **solitons are not stable in this kind of structures**.



# Transport in organic electronic materials

- Charges moving in organic semiconductors create changes in the bond-length alternation pattern.
- Quasi particles: Polarons
  - Polaron: a bound soliton – antisoliton. **The neutral polaron is not stable** since soliton and antisoliton will annihilate.

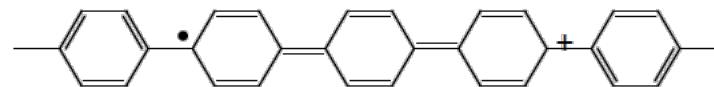


# Transport in organic electronic materials

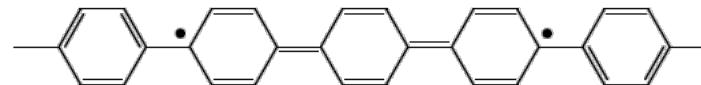
- Quasi particles :
  - Charged polarons: The charge and associated deformation act like a quasi-particle that transport charge across the molecule.

Charge    Spin

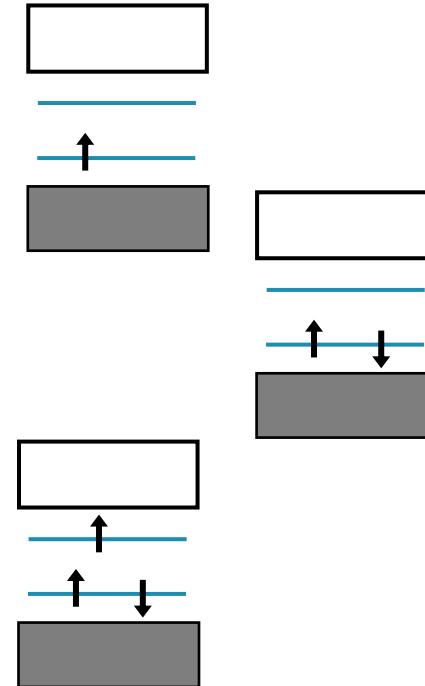
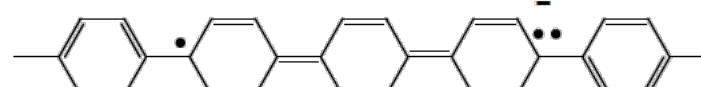
+1             $\frac{1}{2}$



0            0

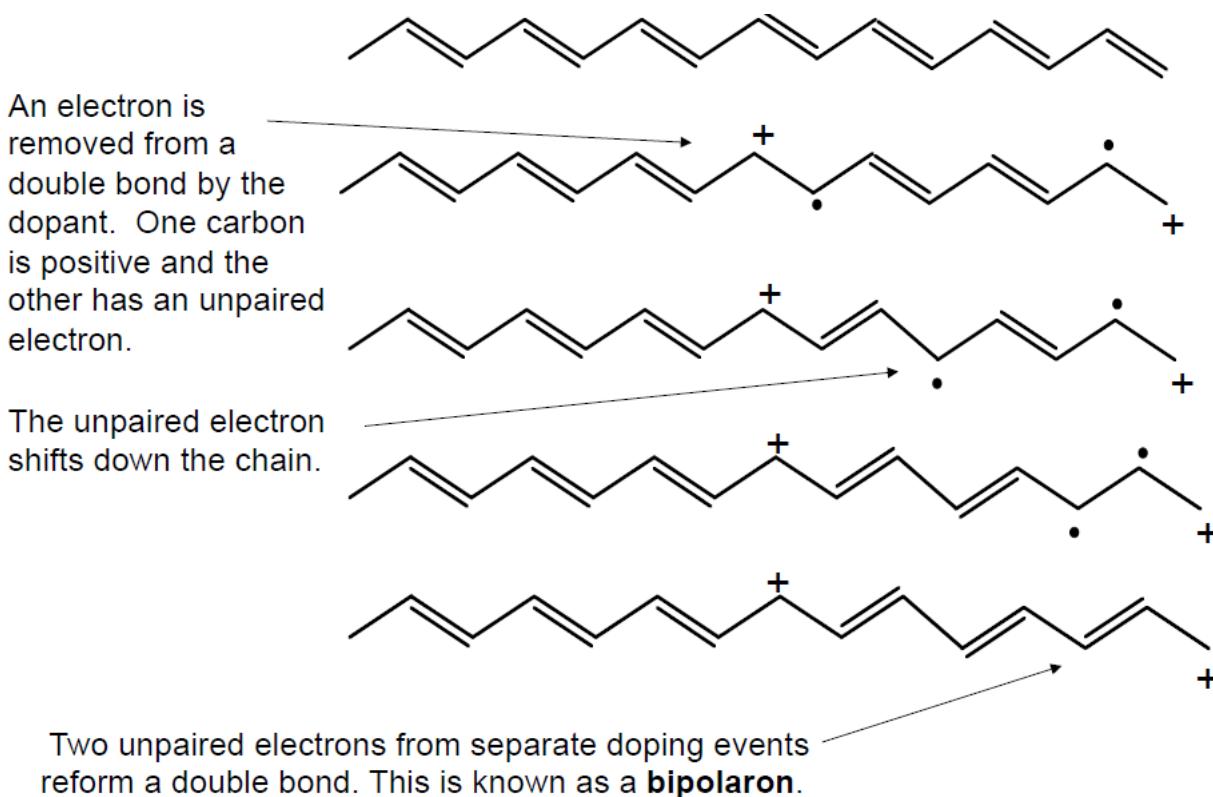


-1             $\frac{1}{2}$



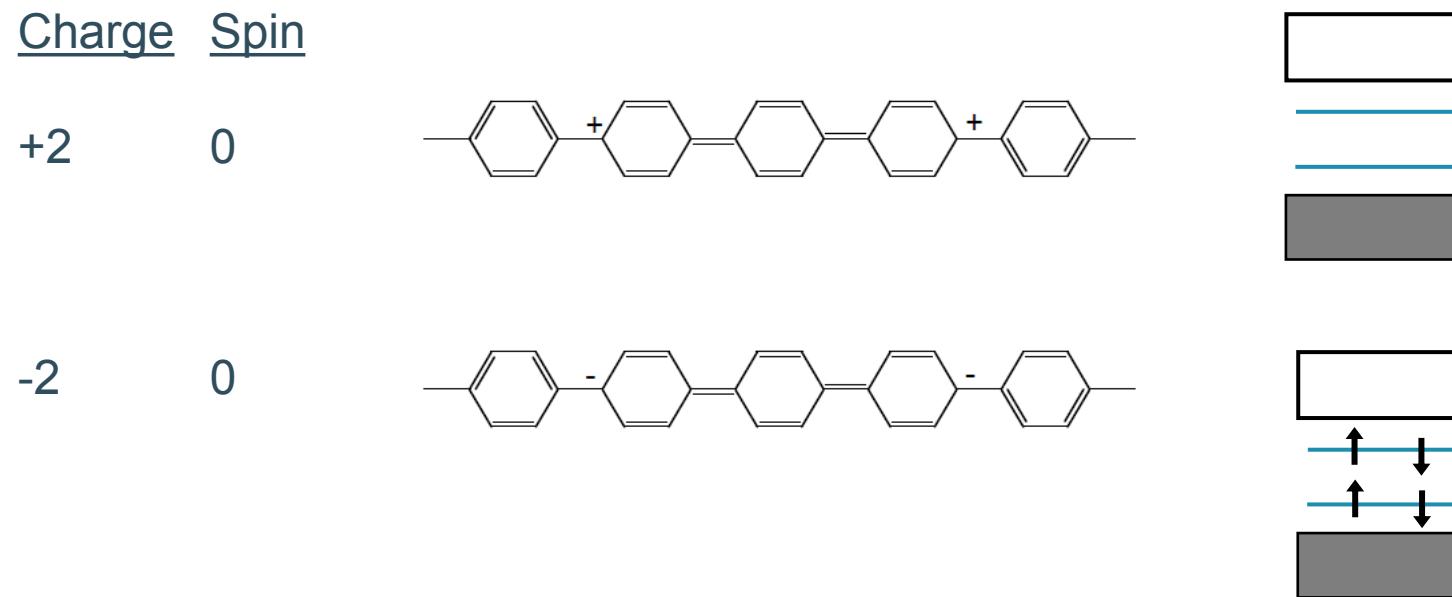
# Transport in organic electronic materials

- Quasi particles:
  - Bipolarons: Are introduced via doping.



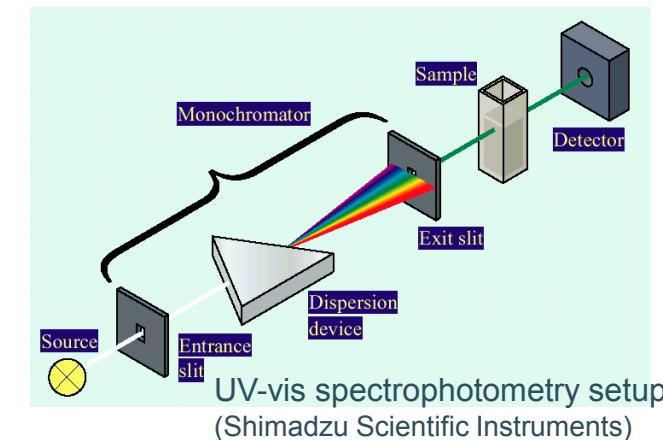
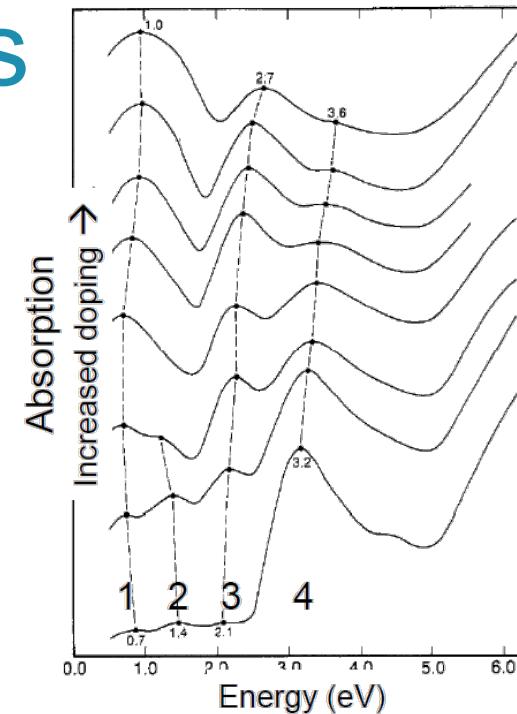
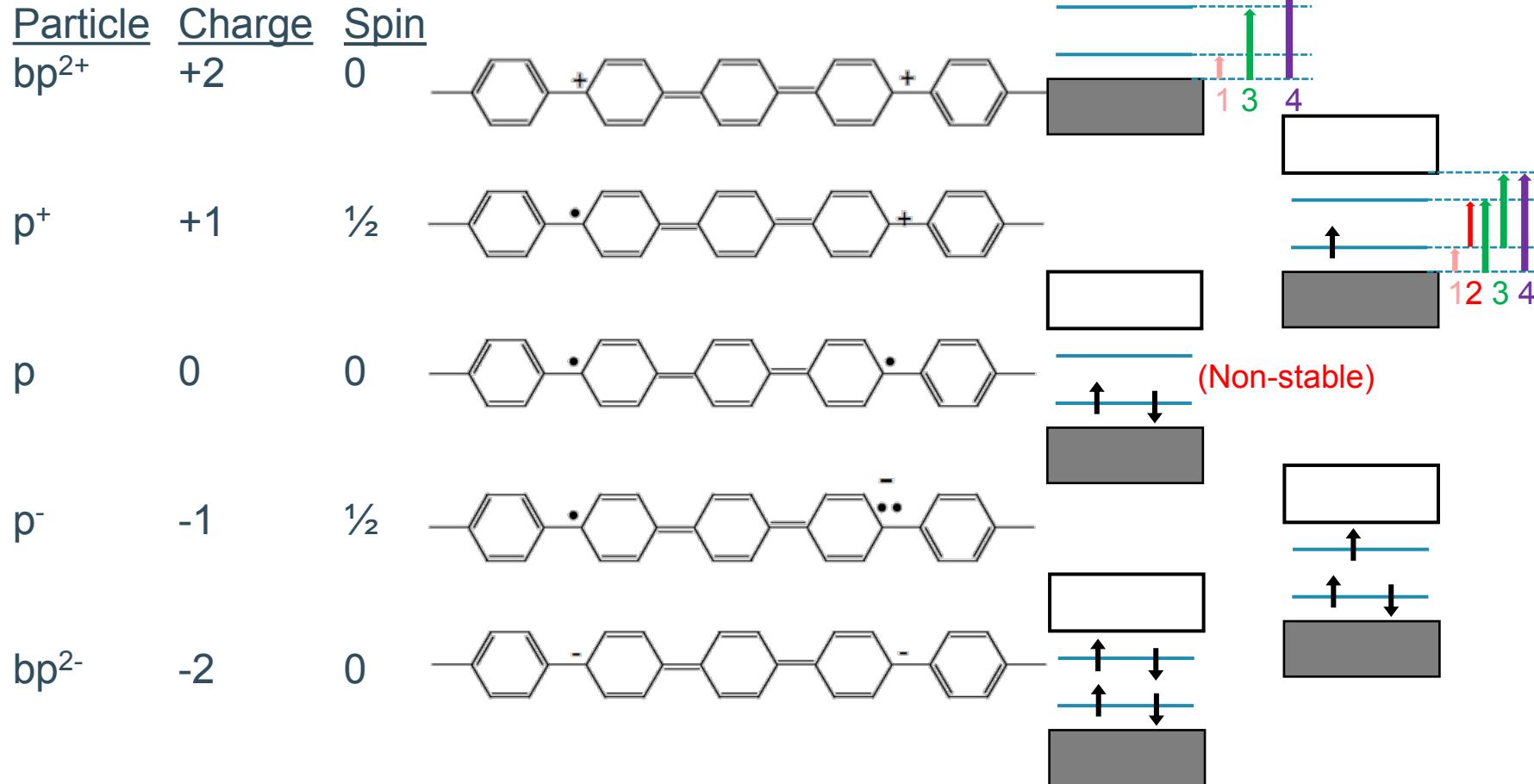
# Transport in organic electronic materials

- Quasi particles :
  - Positively- and negatively-charged bipolarons: they also act as a quasi-particle that transport charge and lattice deformation throughout the molecule.



# Transport in organic electronic materials

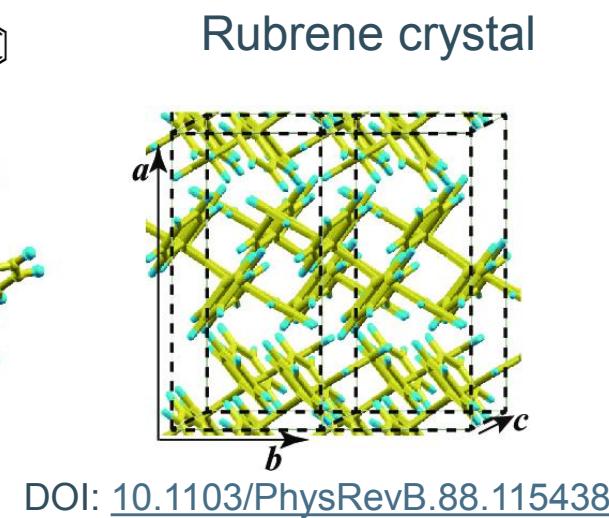
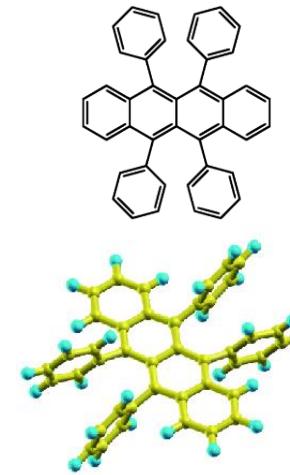
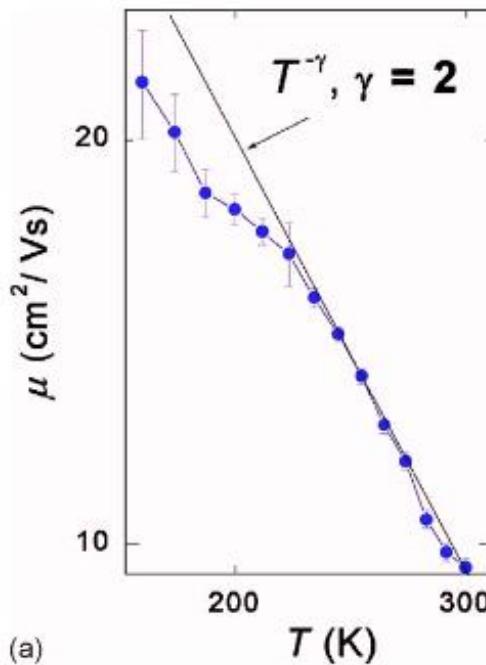
- Quasi particles :



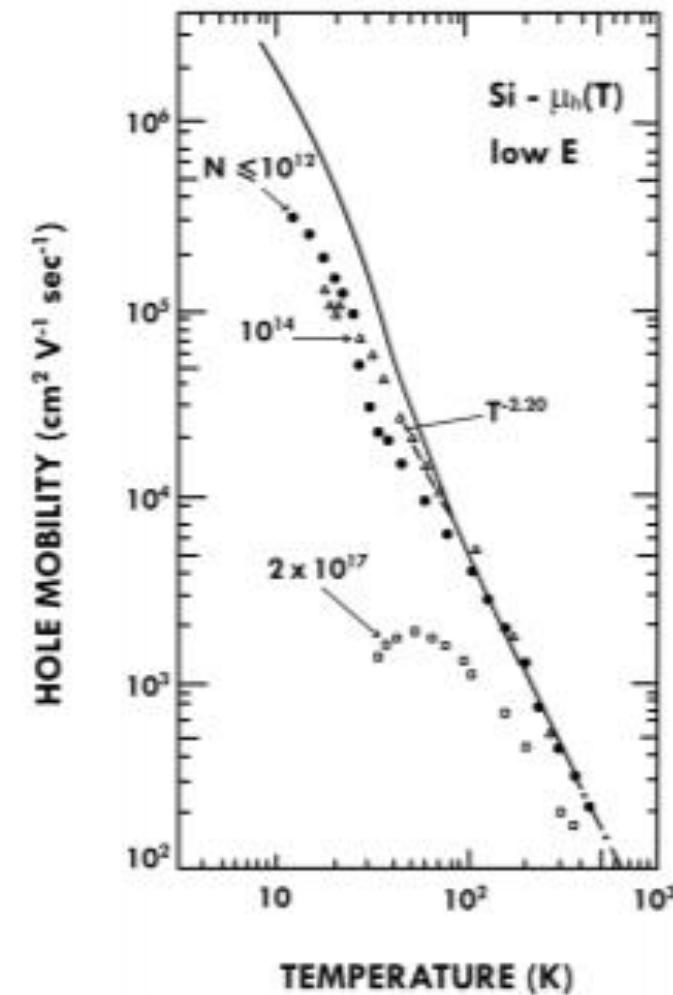
# Transport in organic electronic materials

- Mobility vs temperature: Band-like transport

Reviews of Modern Physics, Volume 78, 2006



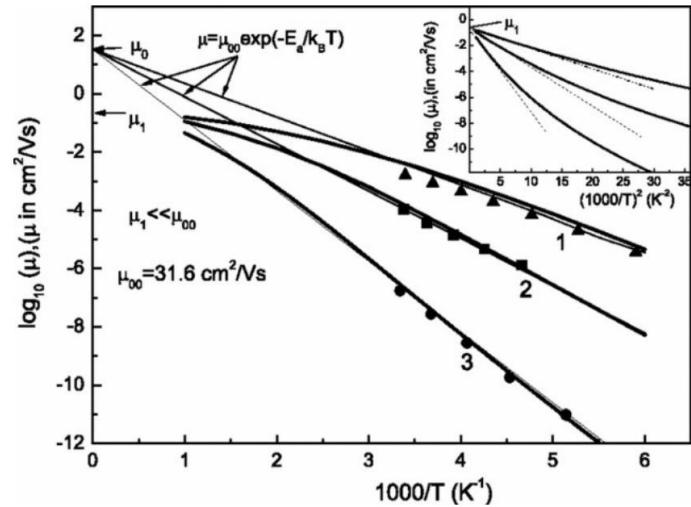
For Si →



Band transport-like behavior observed in highly purified and crystalline organic semiconductors (OSC)

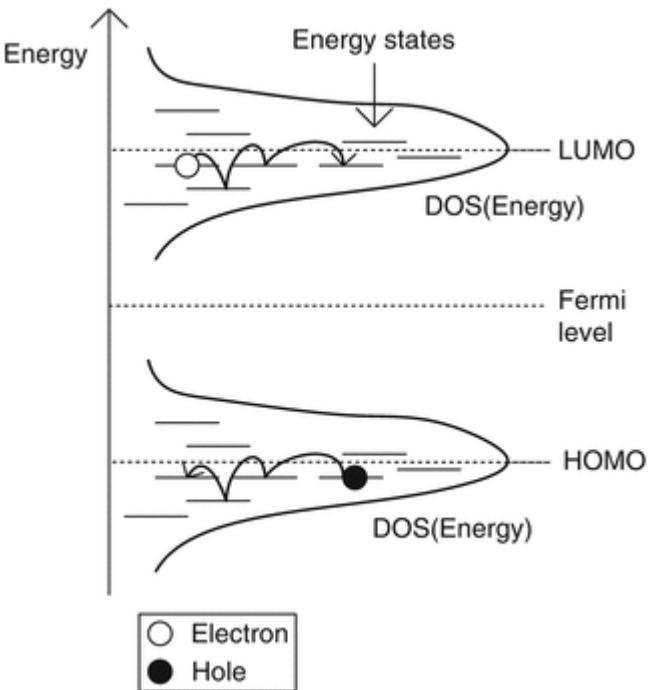
# Transport in organic electronic materials

- Mobility vs temperature: Variable Range Hopping (VRH) Transport
  - But most of the times OSC are too disordered to exhibit band transport behavior.
  - Instead, charge carriers move by hopping from molecule to molecule. The hopping process is thermally activated:



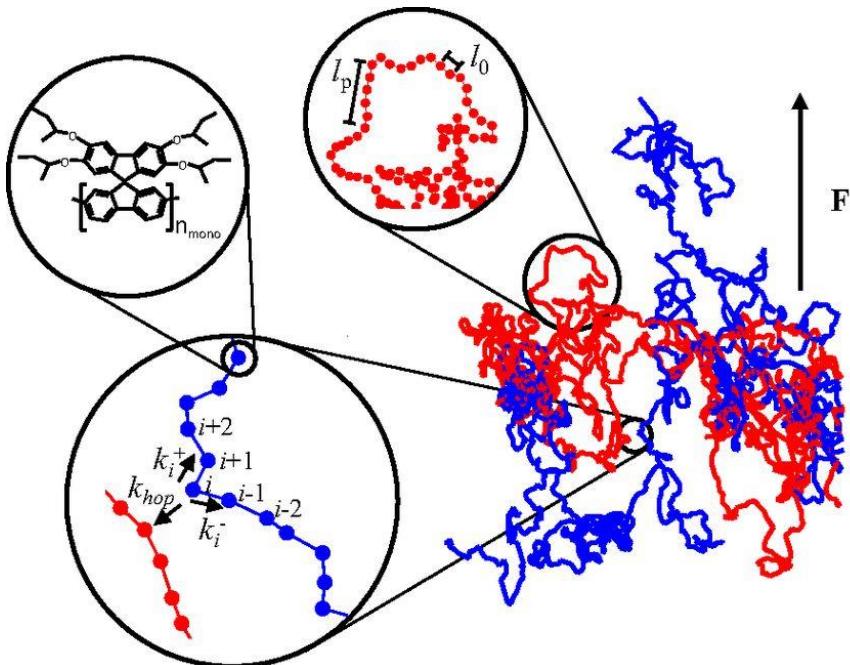
$$\mu \propto \mu_0 e^{-\frac{\Delta E}{k_B T}}$$

Mobility vs  $1/T$  for (1) PCBM, (2) region-regular P3HT, and (3) OC1C11-PPV  
(DOI: 10.1103/PhysRevB.81.045202)

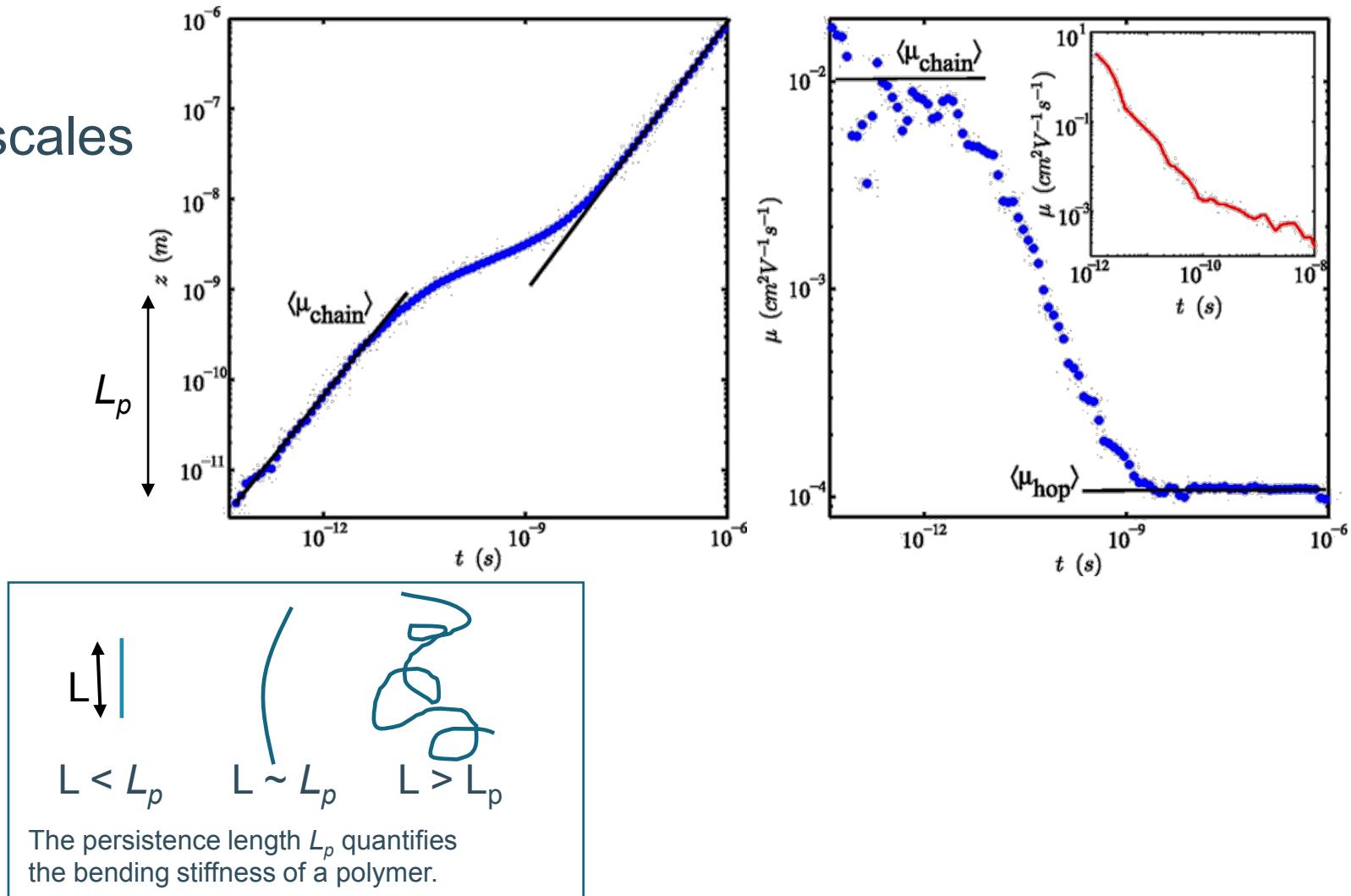


# Transport in organic electronic materials

- Mobility: time and length scales

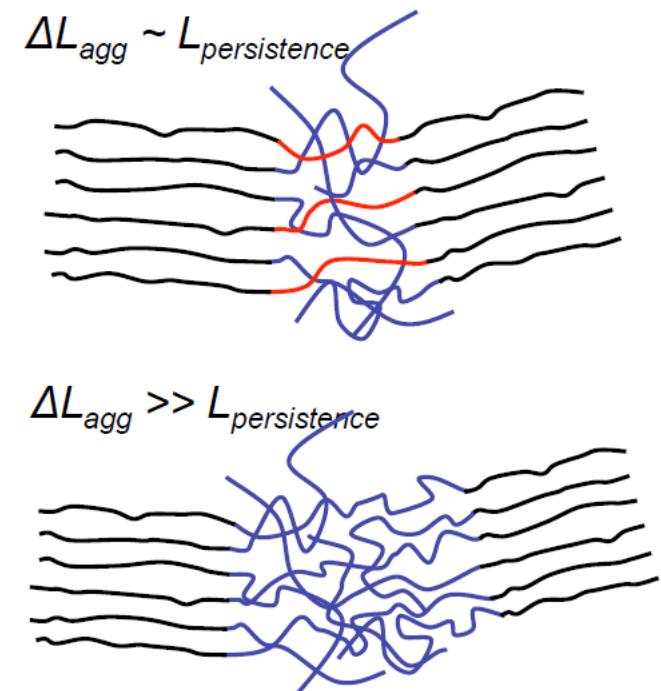
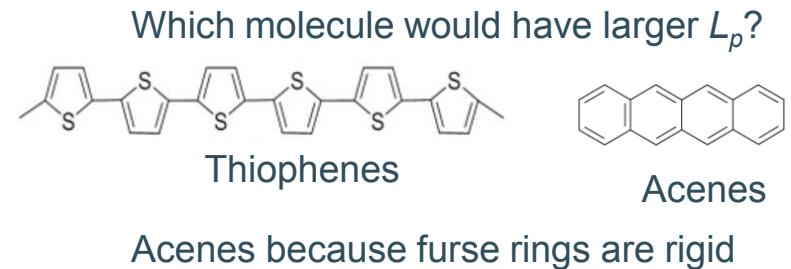
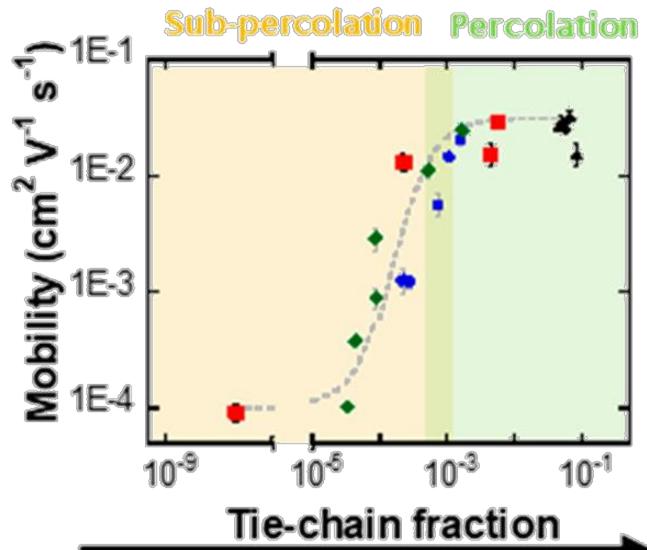
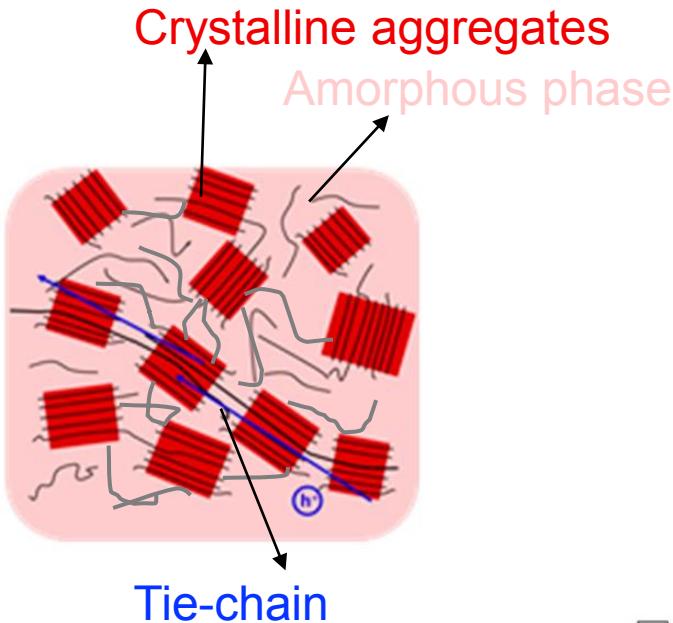


<https://doi.org/10.1073/pnas.1307158110>



# Transport in organic electronic materials

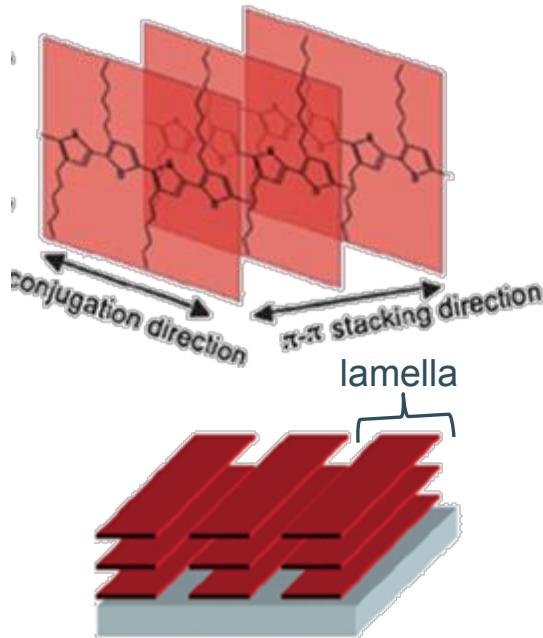
- Mobility: connectivity



If the distance between aggregates  $\Delta L_{agg} \leq L_p \rightarrow$   
Tie-chain can bridge efficiently → **High mobility**

# Transport in organic electronic materials

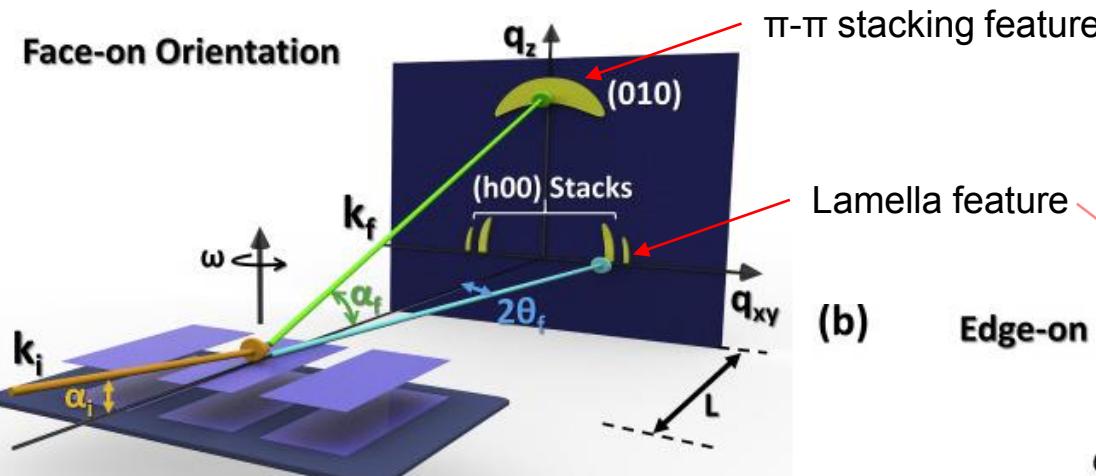
- How to measure crystallinity: Grazing incidence wide angle X-ray scattering (GIWAXS patterns).



Formation of polymer lamella

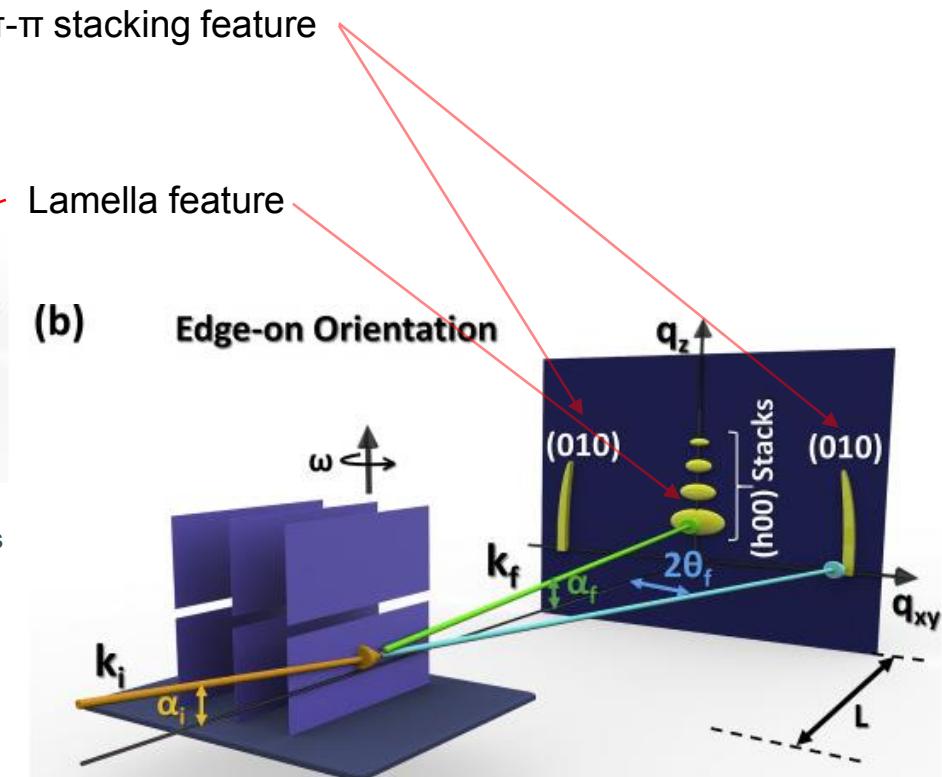
(Polym. Chem., 2013, 4, 5197-5205,  
<https://doi.org/10.1039/C3PY00131H>)

(a)



Materials Today Advances 8 (2020) 100086 Contents

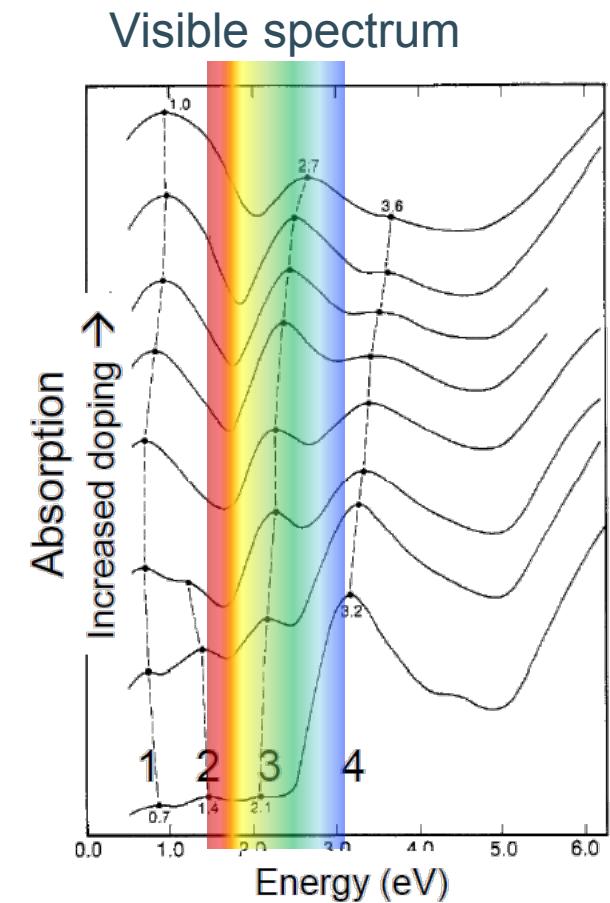
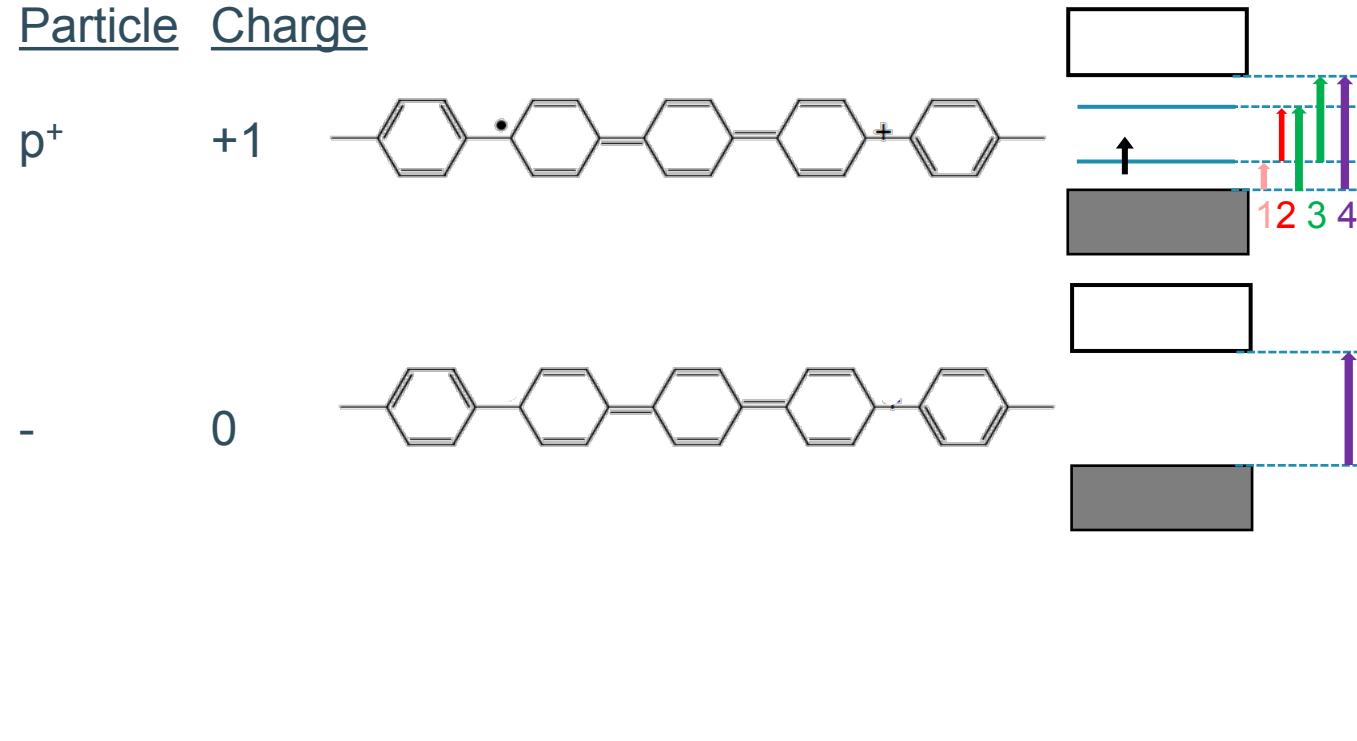
(b)



# Applications of organic electronic materials

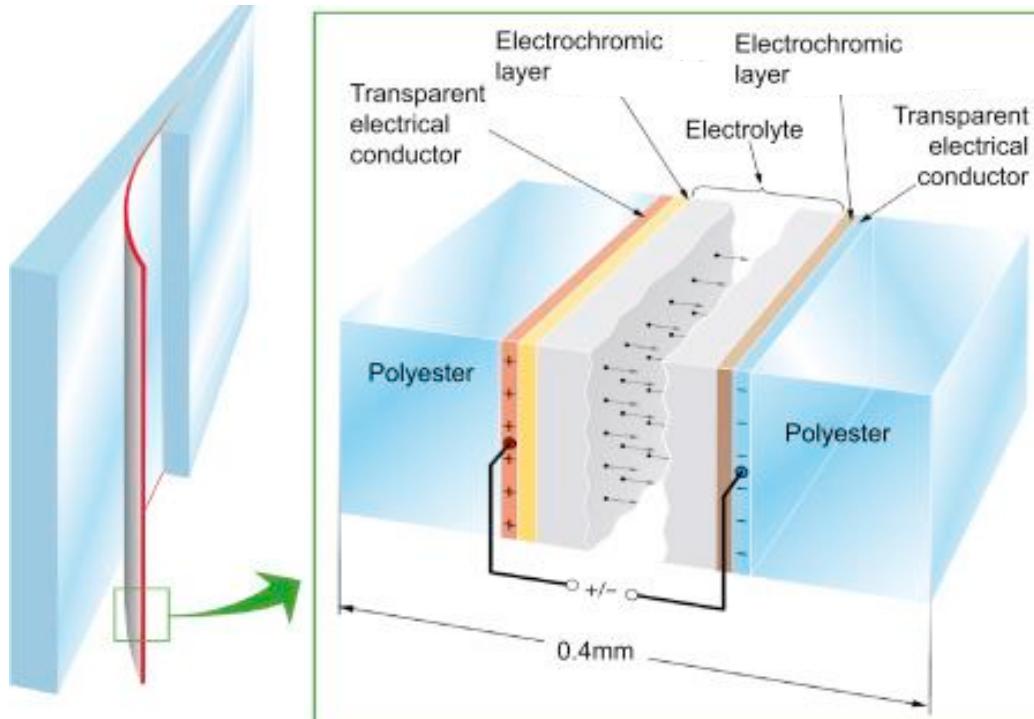
# Transport in organic electronic materials

- Electrochromic devices (ECs): Controlled doping of the material introduce visible light absorption by polarons

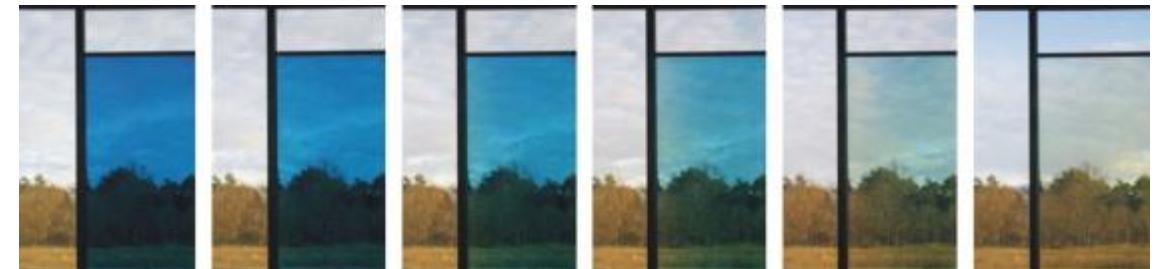


# Transport in organic electronic materials

- Electrochromic devices (ECs): More visible light absorption by polarons -> “darker glasses” activated electrically



<https://doi.org/10.1016/B978-0-12-811091-1.00008-2>



Gesimat, 2009, retrieved April 14, 2009

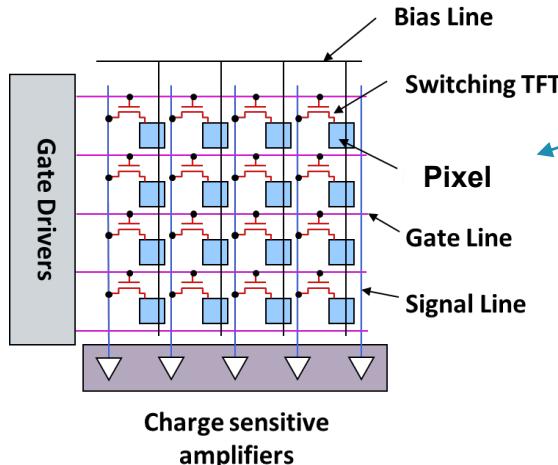
# Applications of organic electronic materials

- Organic field effect transistors (OFETs)
  - Historical evolution

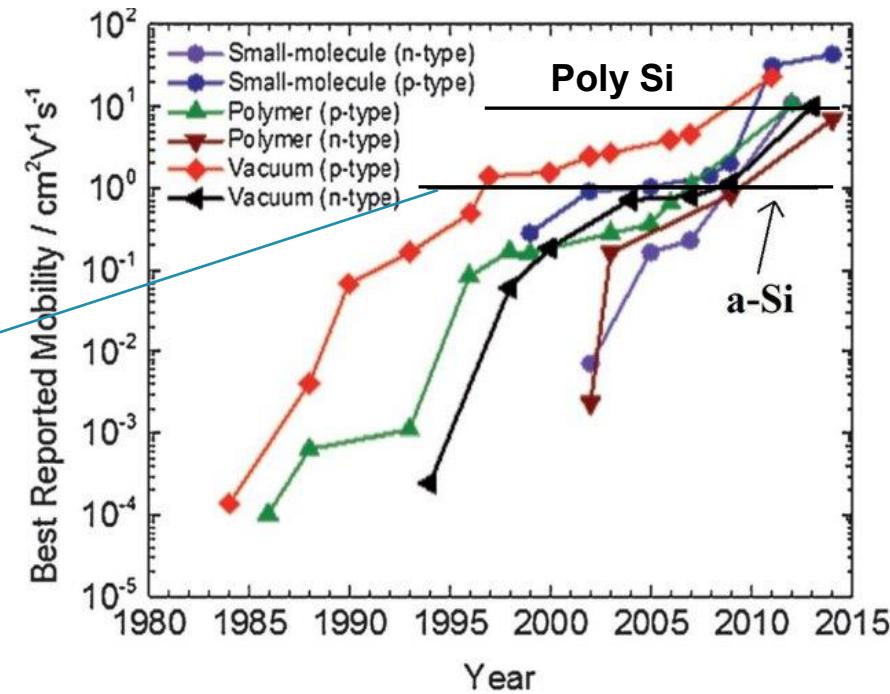
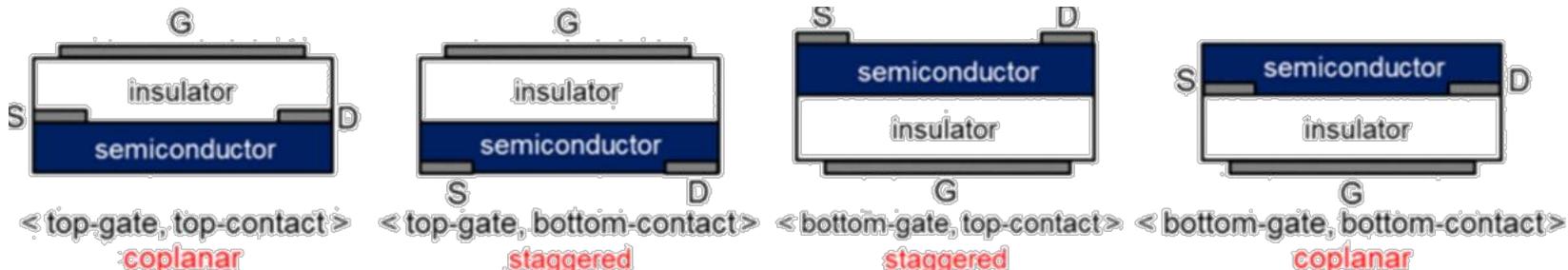
Active-matrix displays are possible with OFETs  
Frequency  $\propto \mu$



K. Myny, et al., *IEEE J. Solid State Circ.* 2012, **47**, 284.



- Structures

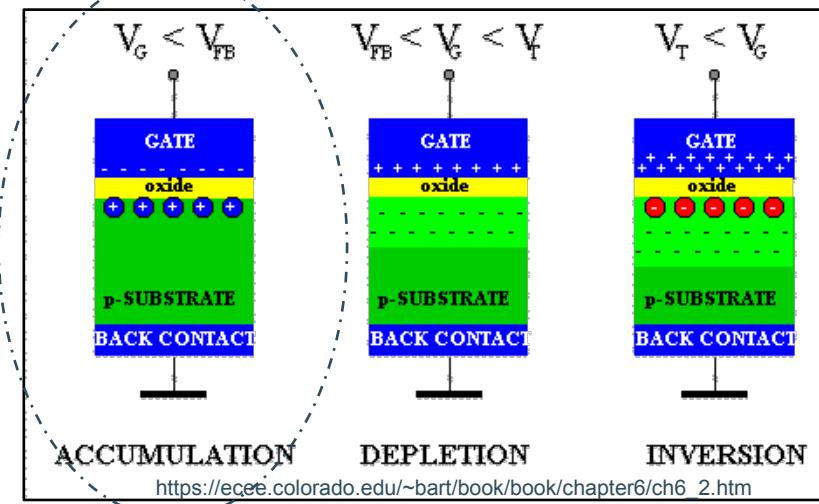
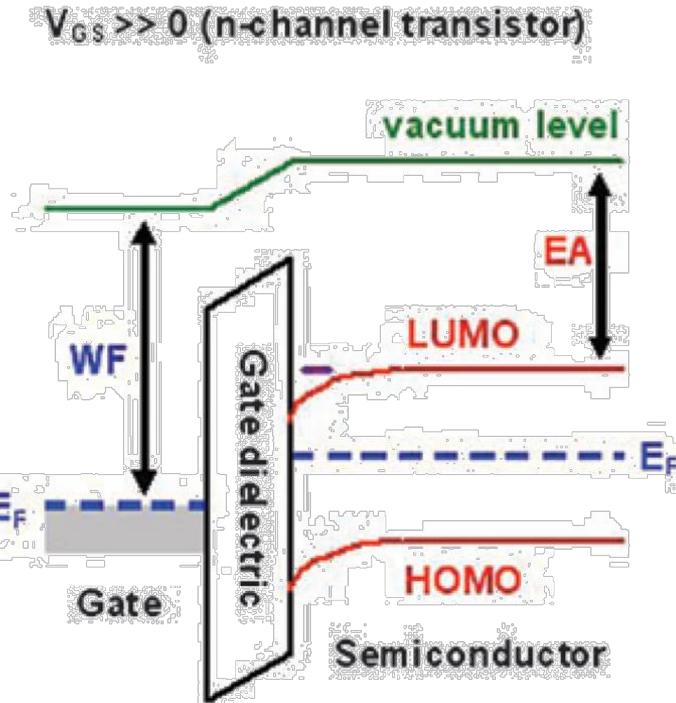
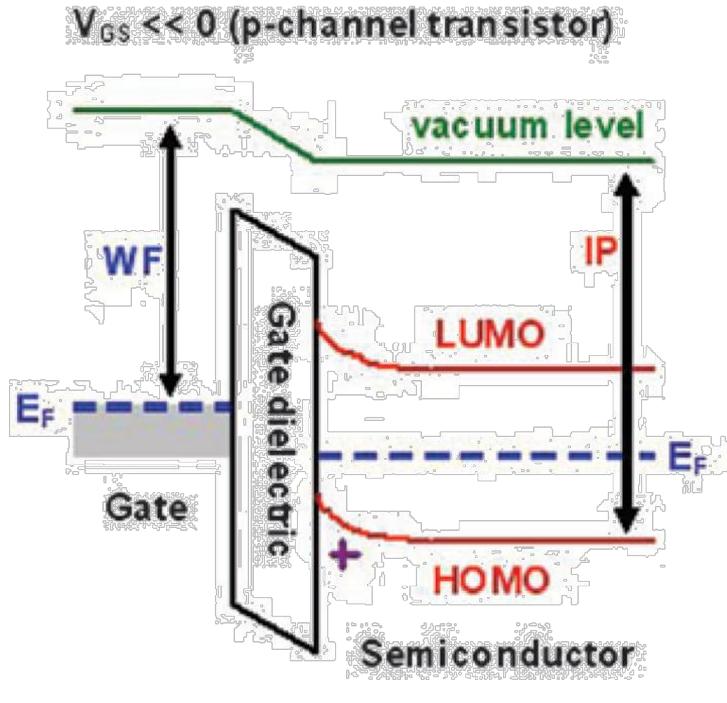


<https://doi.org/10.1002/cphc.201402757>

DOI: 10.1109/TED.2012.2226887

# Applications of organic electronic materials

- Organic field effect transistors (OFETs)
  - P-type vs n-type: contrary to inorganic FETs, OFETs work in accumulation bias regime.

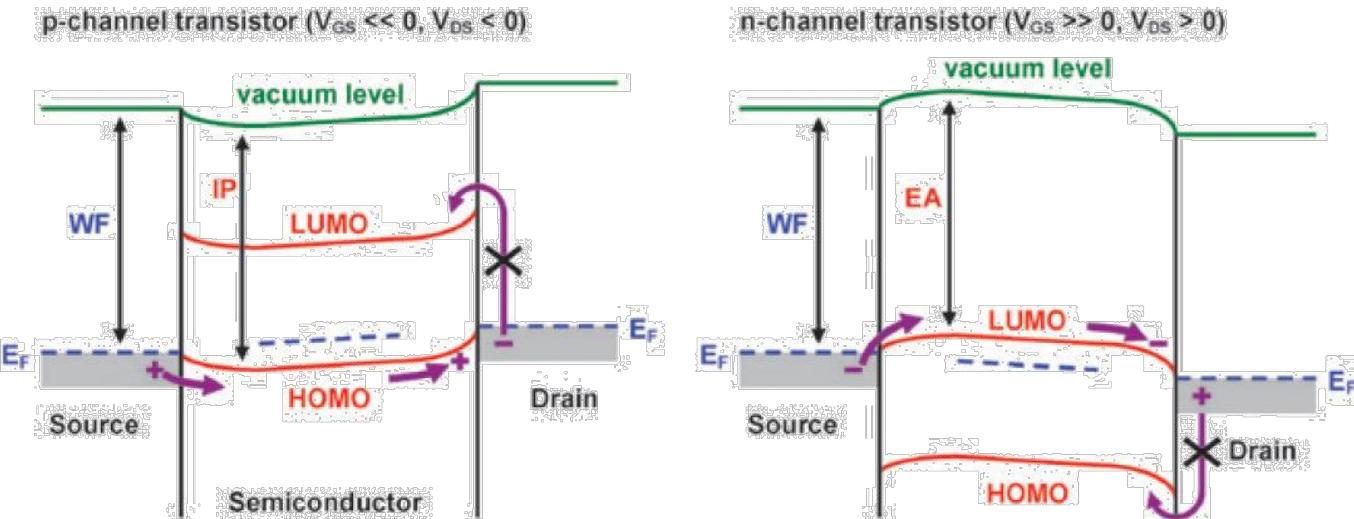


WF: Work function  
EA: Electron affinity  
IP: Ionization potential

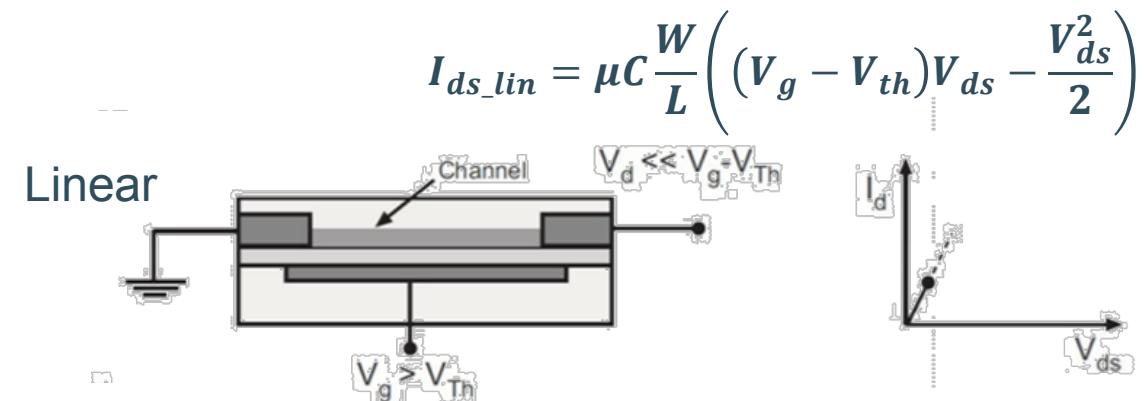
Chem. Soc. Rev., 2010, 39, 2643–2666

# Applications of organic electronic materials

- Organic field effect transistors (OFETs)
  - Operation regimes



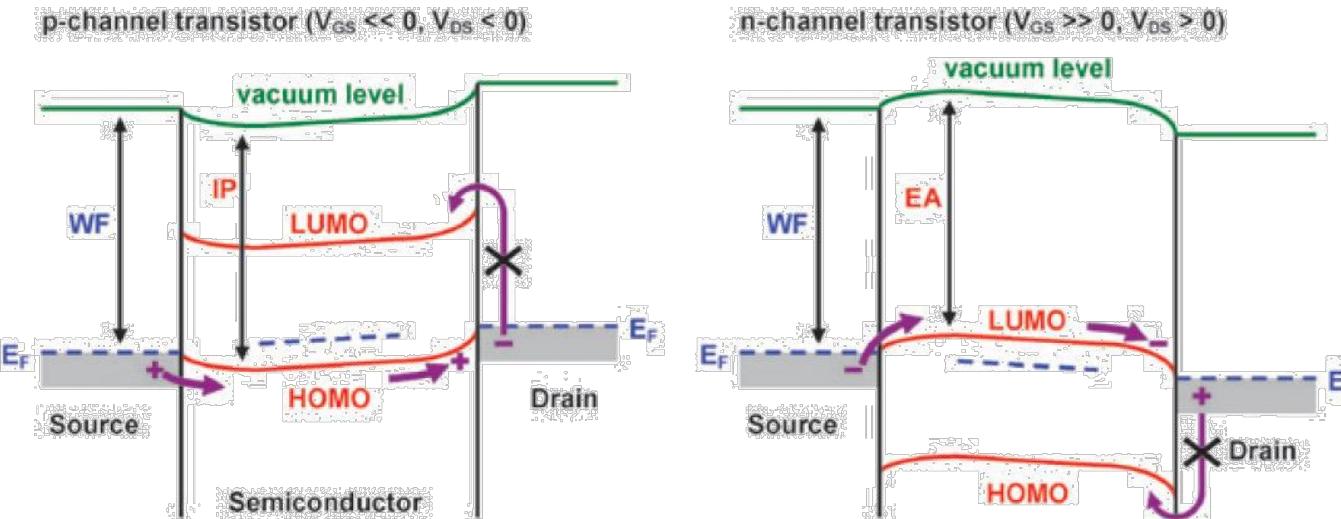
Chem. Soc. Rev., 2010, 39, 2643–2666



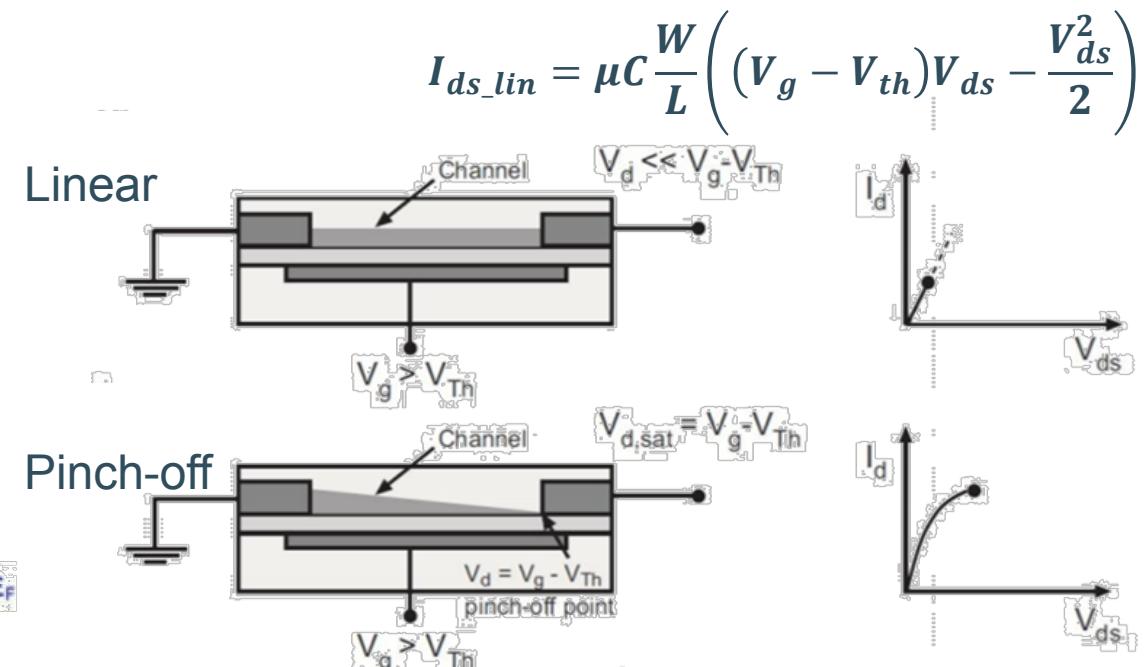
Unravelling Structure-Function Relationships in High Mobility  
Donor-Acceptor Co-Polymers, Thesis 2017, Monash University

# Applications of organic electronic materials

- Organic field effect transistors (OFETs)
  - Operation regimes



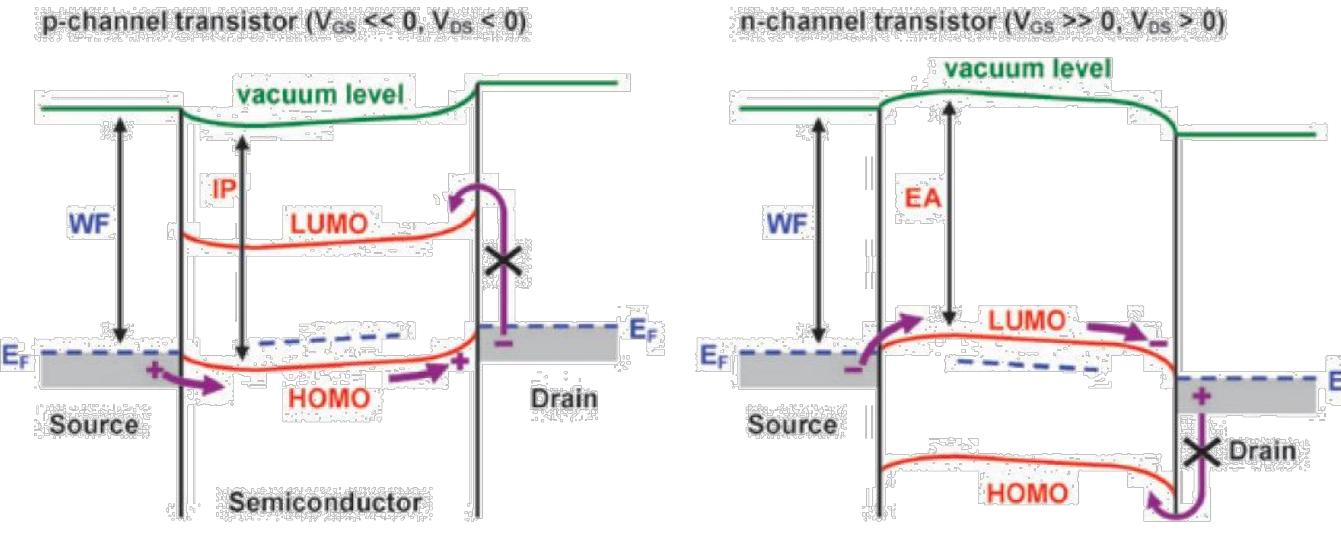
Chem. Soc. Rev., 2010, 39, 2643–2666



Unravelling Structure-Function Relationships in High Mobility  
Donor-Acceptor Co-Polymers, Thesis 2017, Monash University

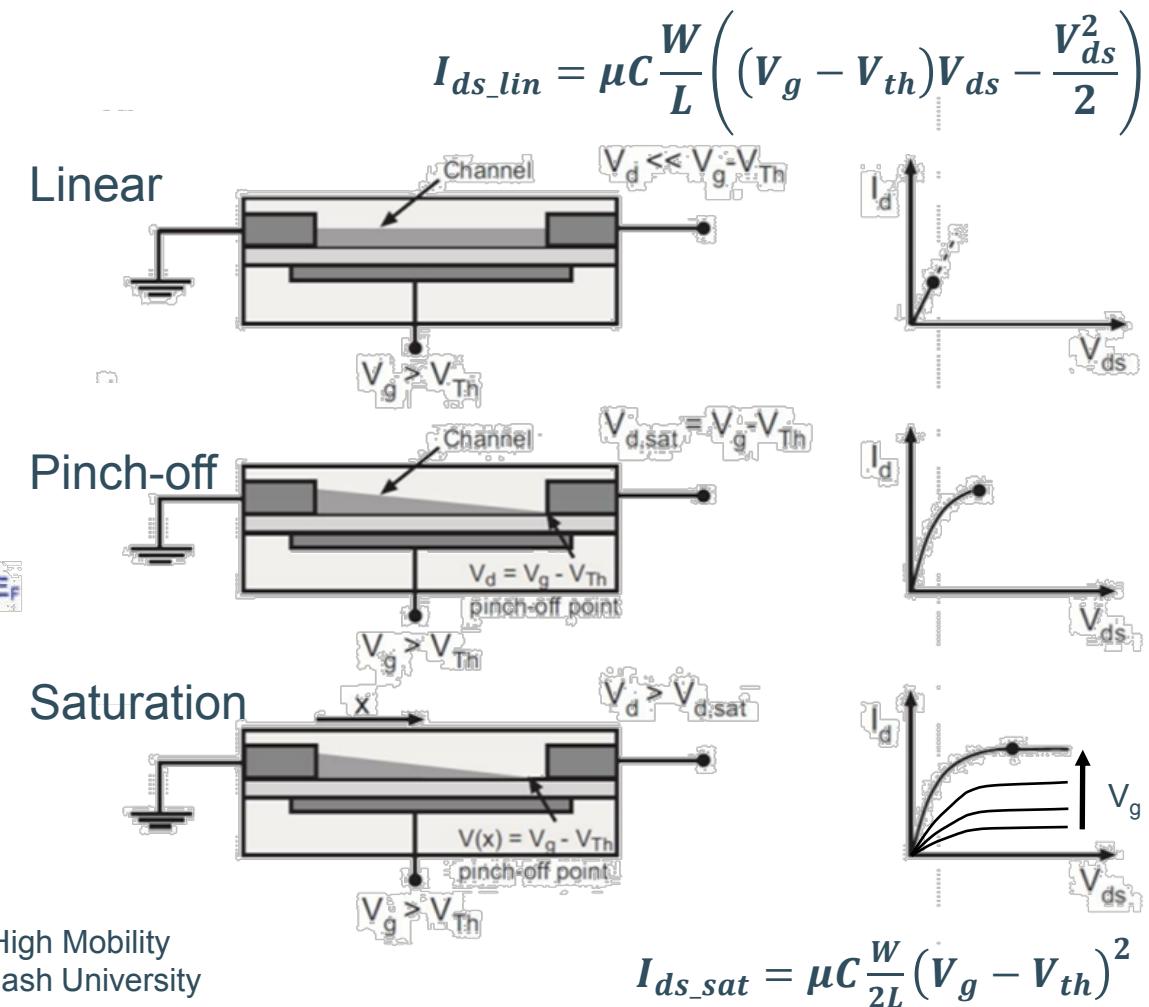
# Applications of organic electronic materials

- Organic field effect transistors (OFETs)
  - Operation regimes



Chem. Soc. Rev., 2010, 39, 2643–2666

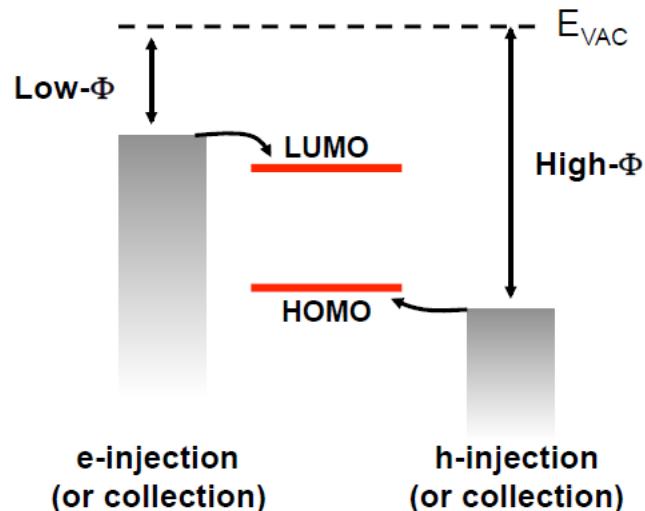
Unravelling Structure-Function Relationships in High Mobility  
Donor-Acceptor Co-Polymers, Thesis 2017, Monash University



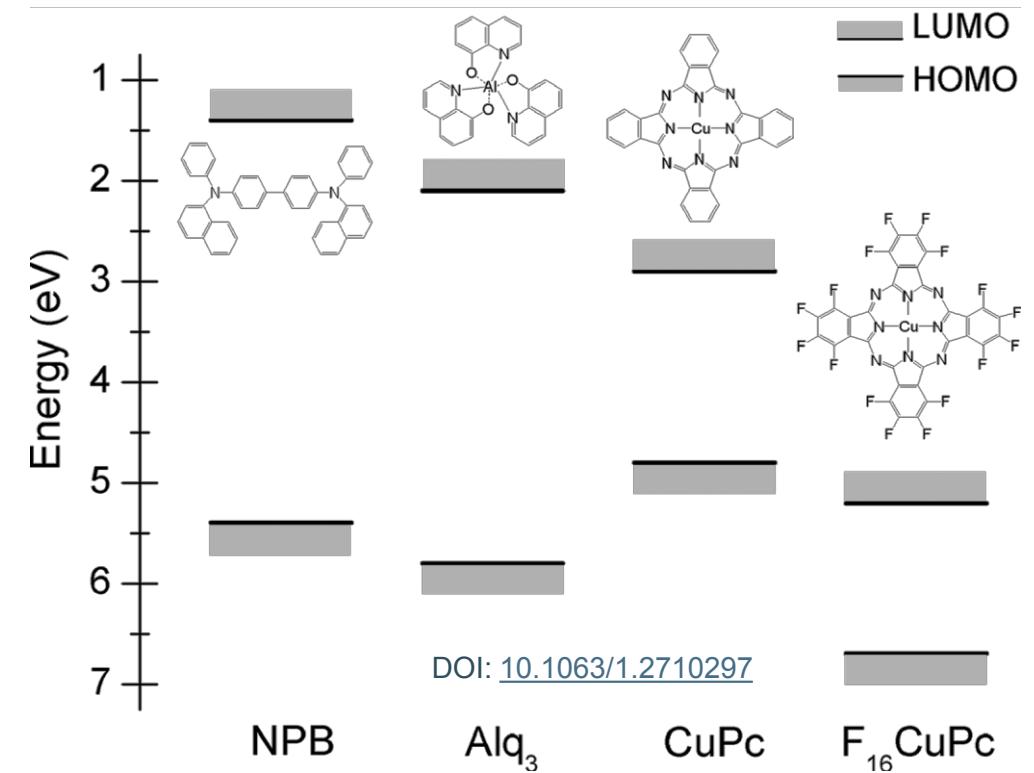
# Applications of organic electronic materials

- Organic field effect transistors (OFETs)
    - Contacts. Material is defined by the HOMO LUMO level to avoid energy barriers

| <b>Element</b> | <b>Work function <math>\Phi</math></b> |
|----------------|--|
| Cs             | 2.14                                   |
| K              | 2.30                                   |
| <b>Ba</b>      | 2.70                                   |
| Na             | 2.75                                   |
| <b>Ca</b>      | 2.87                                   |
| Li             | 2.90                                   |
| Mg             | 3.66                                   |
| In             | 4.12                                   |
| Ag             | 4.26                                   |
| Al             | 4.28                                   |
| Nb             | 4.30                                   |
| Cr             | 4.50                                   |
| Cu             | 4.65                                   |
| Si             | 4.85                                   |
| Au             | 5.10                                   |
| Pt             | 5.60                                   |



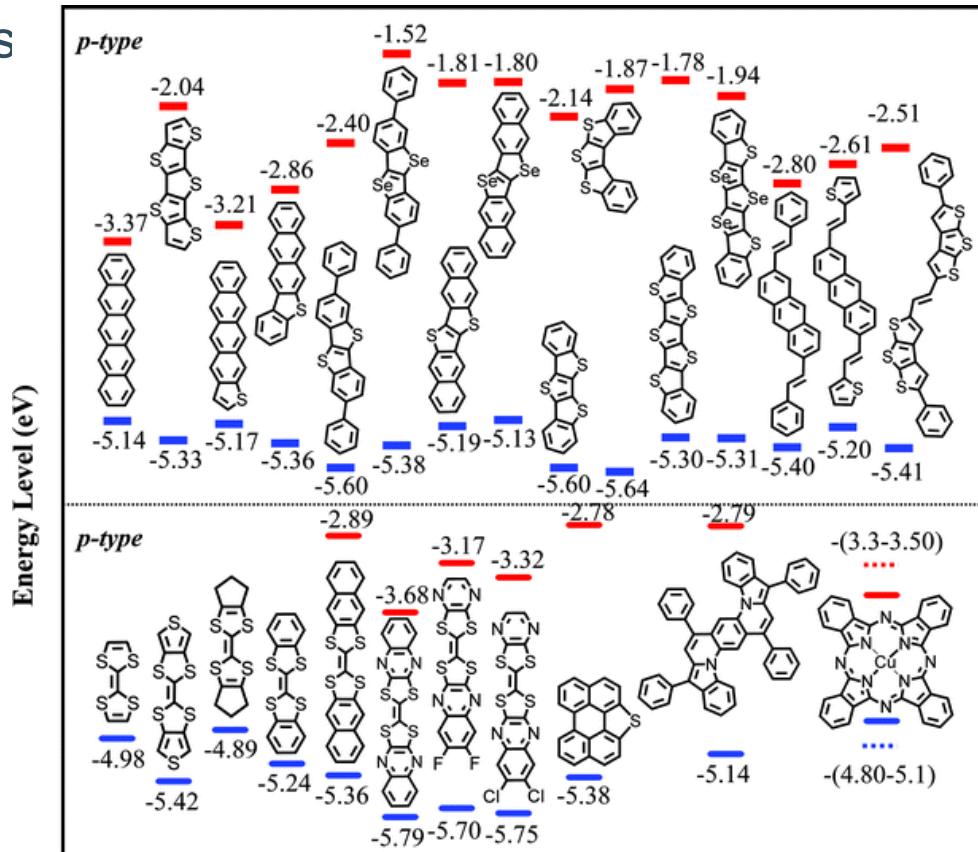
**Charge injection or collection in all devices depends on the relative band alignment of the semiconductor and the electrode materials**



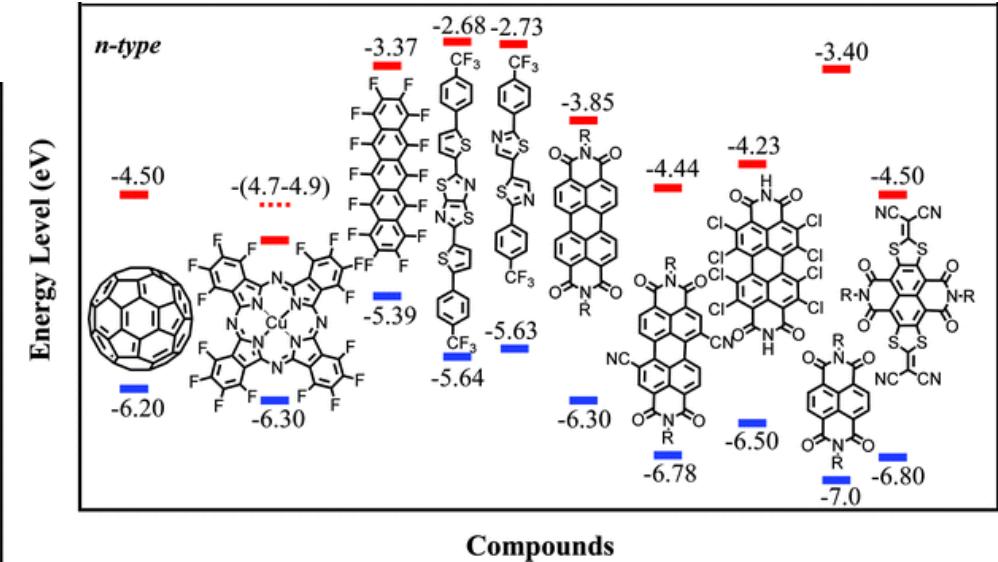
# Applications of organic electronic materials

- Organic field effect transistors (OFETs)

- Contacts



DOI: 10.1039/c0cc00947d



There are not so many good-performing n-type materials that aligned well with stable metals -> **Most OFETs performing well are p-type!**

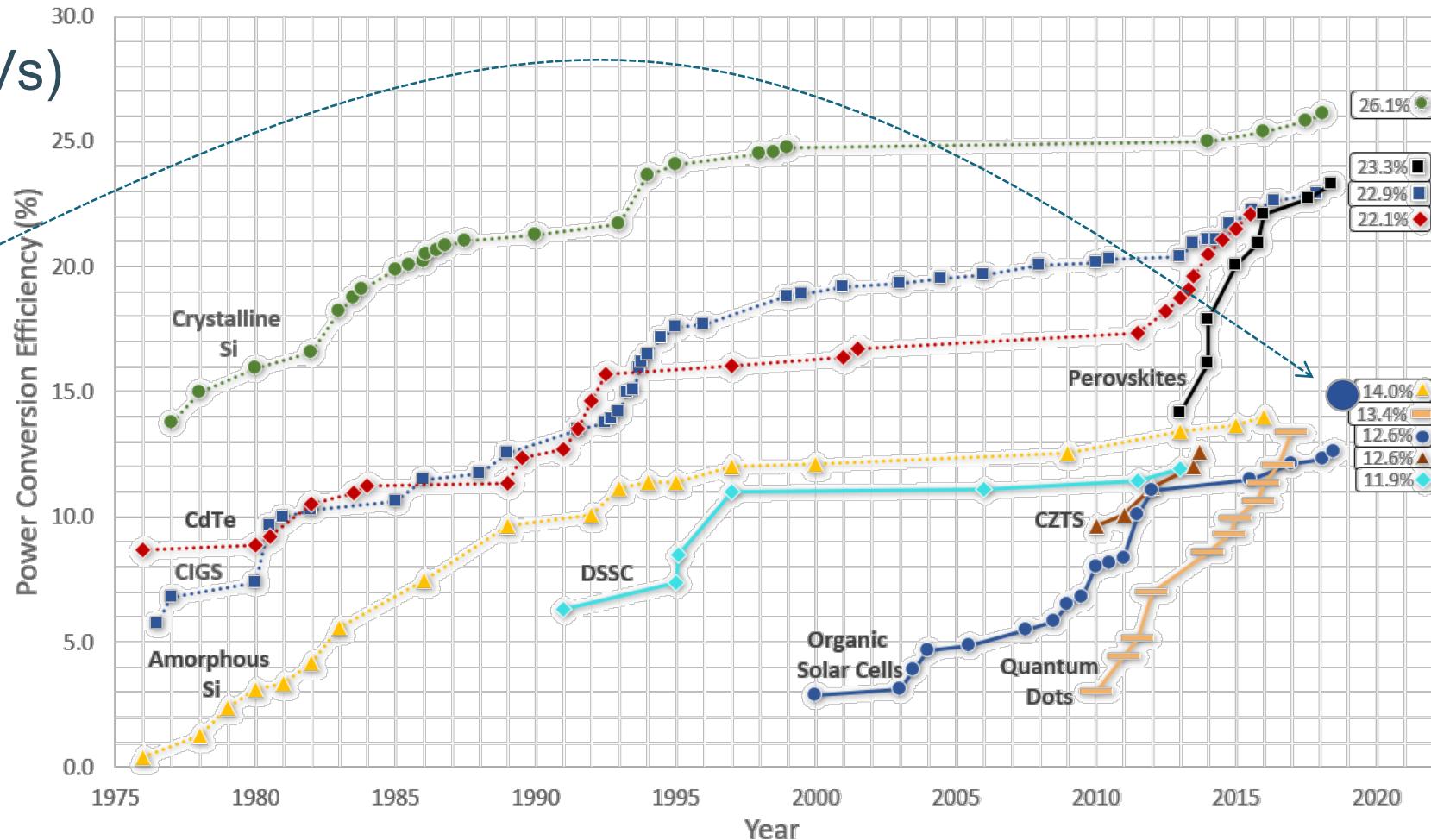
# Applications of organic electronic materials

- Organic solar cells (OPVs)
  - Historical evolution



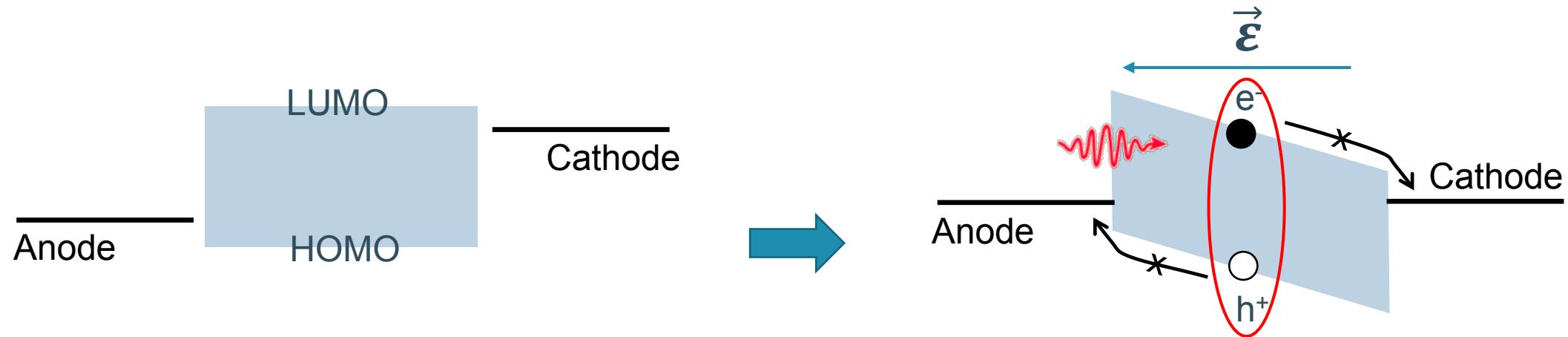
A fair comparison for all scenarios?

- Cells are rated at 1 sun, normal incidence and 25 °C.
- OPV holds performance better than Si at **low light and low angles** (opportunity indoors)
- OPVs performance degrades less than Si performance at **high temperature**



# Applications of organic electronic materials

- Organic solar cells (OPVs): They convert optical energy into electrical energy



**Exciton:** quasi particle composed of a bound electron-hole pair

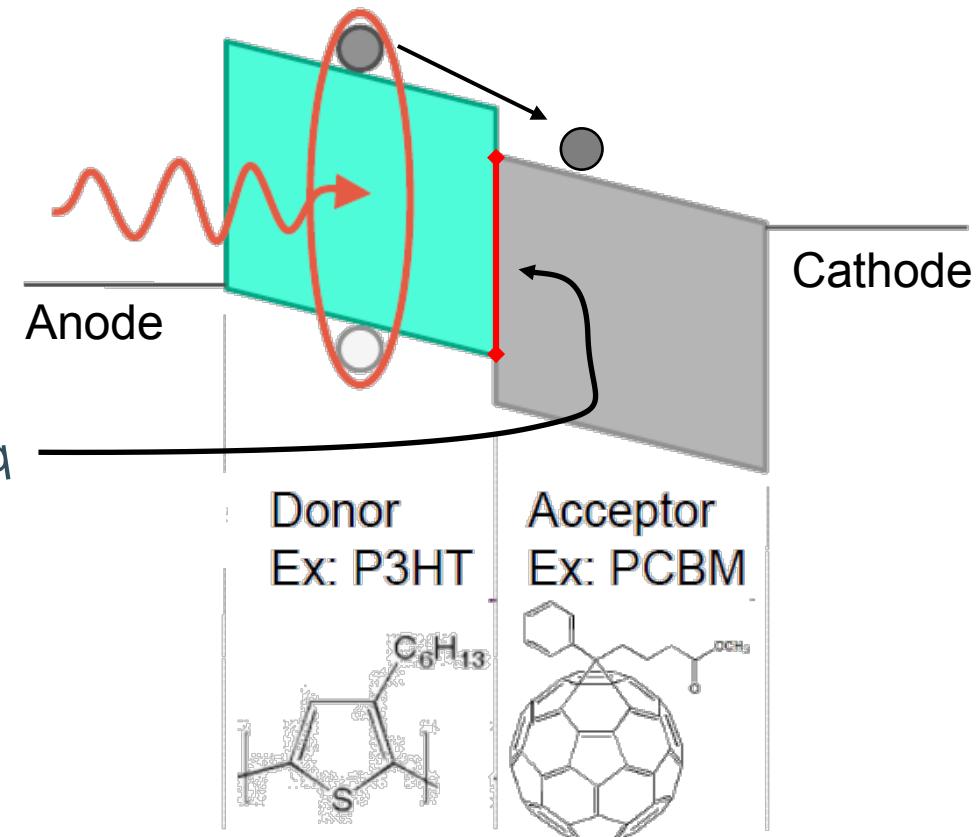
The exciton binding energy in inorganic semiconductors is only  $\sim$  meV, but in organic is up to 0.5 eV. The exciton does not split and the charges don't get collected at the electrodes.

A donor/acceptor heterojunction is needed to provide the internal electrochemical driving force for exciton dissociation.

# Applications of organic electronic materials

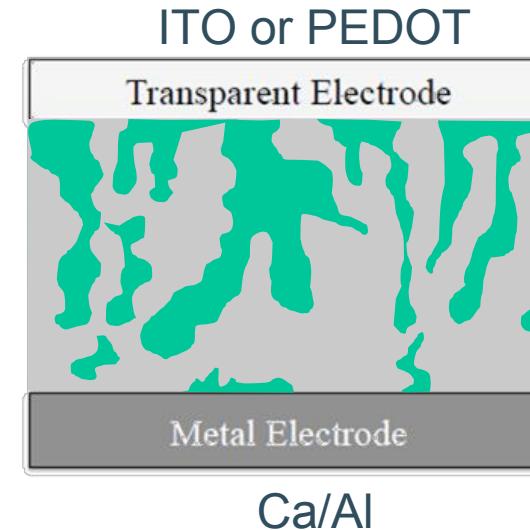
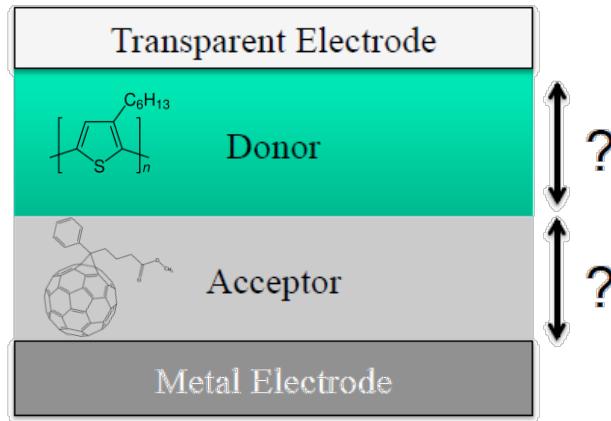
- Organic solar cells (OPVs): Structure
  1. Light absorption
  2. Exciton formation
  3. Exciton splitting
  4. Charge extraction

$$V_{out, max} = (E_{LUMO, acceptor} - E_{HOMO, donor})/q$$



# Applications of organic electronic materials

- Organic solar cells (OPVs): Structure

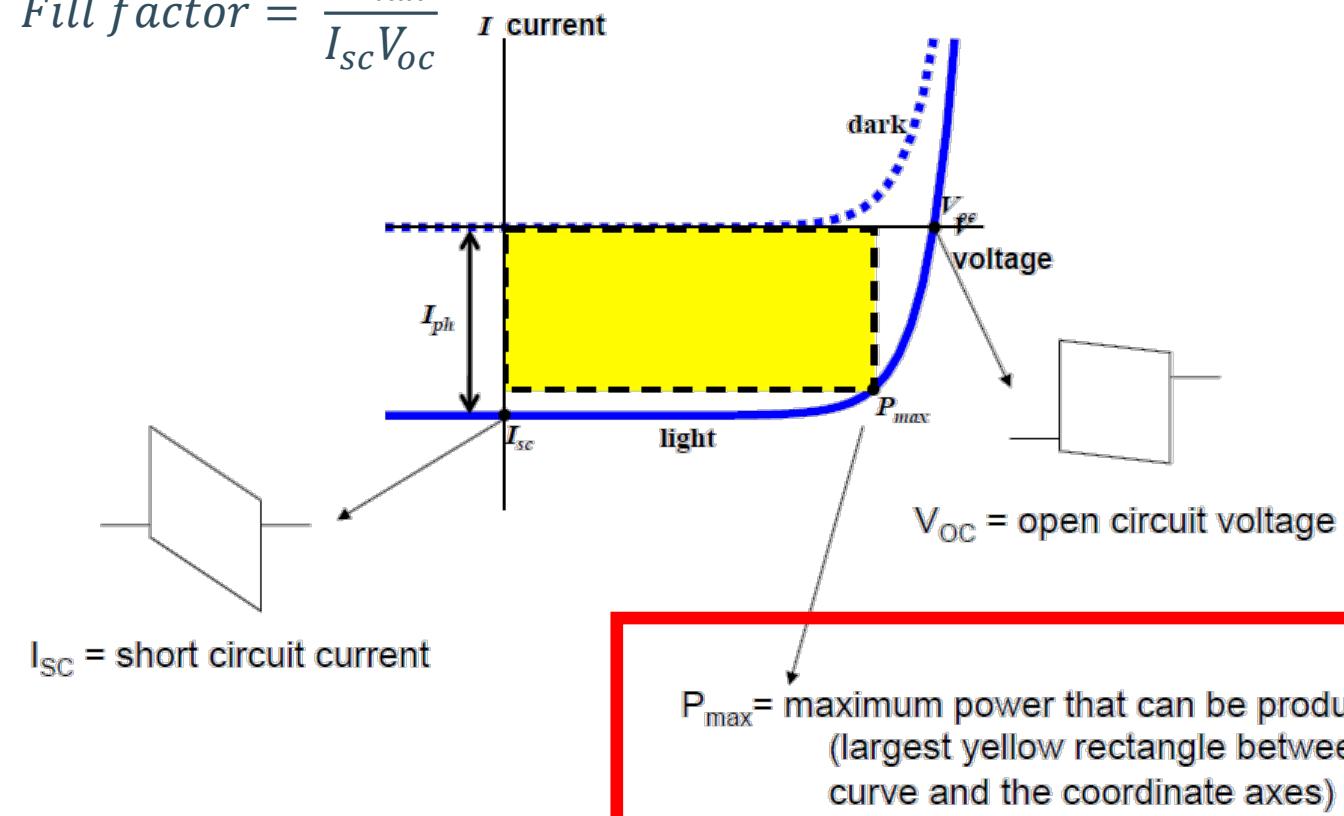


- The thickness of the material should be at least 100 nm to absorb most of the light
- However, the exciton mean free path (before recombination) is only 10 nm
- It is necessary to split the exciton (reach a D/A interface) before it recombines!  
-> Bulk heterojunction morphology: allow thick layers with many interfaces everywhere

# Applications of organic electronic materials

- Organic solar cells (OPVs): Performance

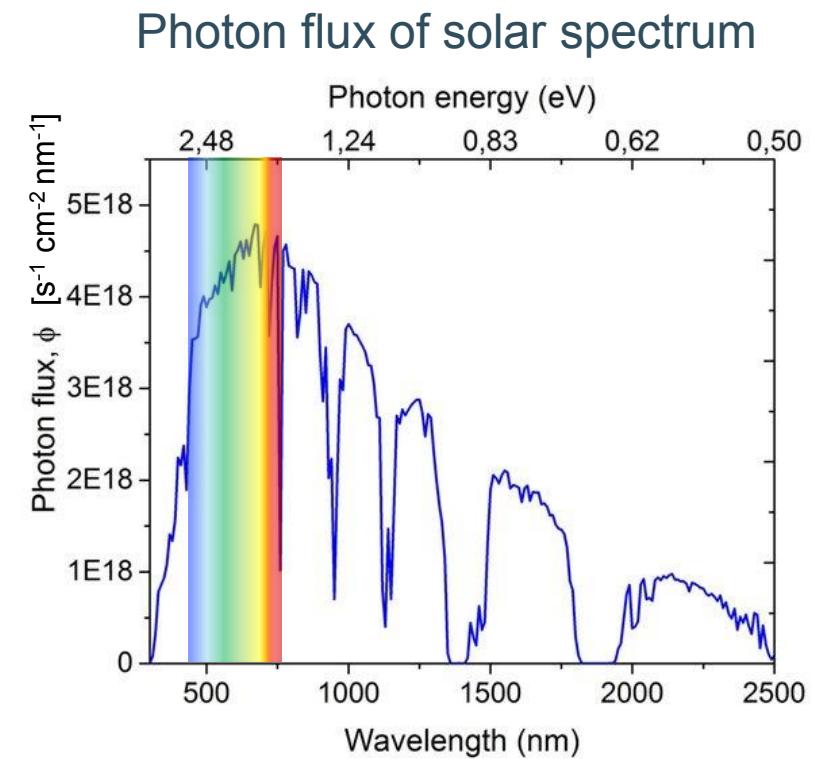
$$\text{Fill factor} = \frac{P_{max}}{I_{sc}V_{oc}}$$



# Applications of organic electronic materials

- Organic solar cells (OPVs): Efficiency
  - Internal quantum efficiency (IQE)  
(Photons ABSORBED / electrons out)
  - External quantum efficiency (EQE)  
(Rate of photons arriving to the device / rate of electrons out)  
Or incident photon to converted electron (IPCE)
- $J_{sc} = q \int EQE(\lambda) PhotonFlux(\lambda) d\lambda$
- IQE & EQI <1, IQE>EQI
- Power conversion efficiency (PCE)

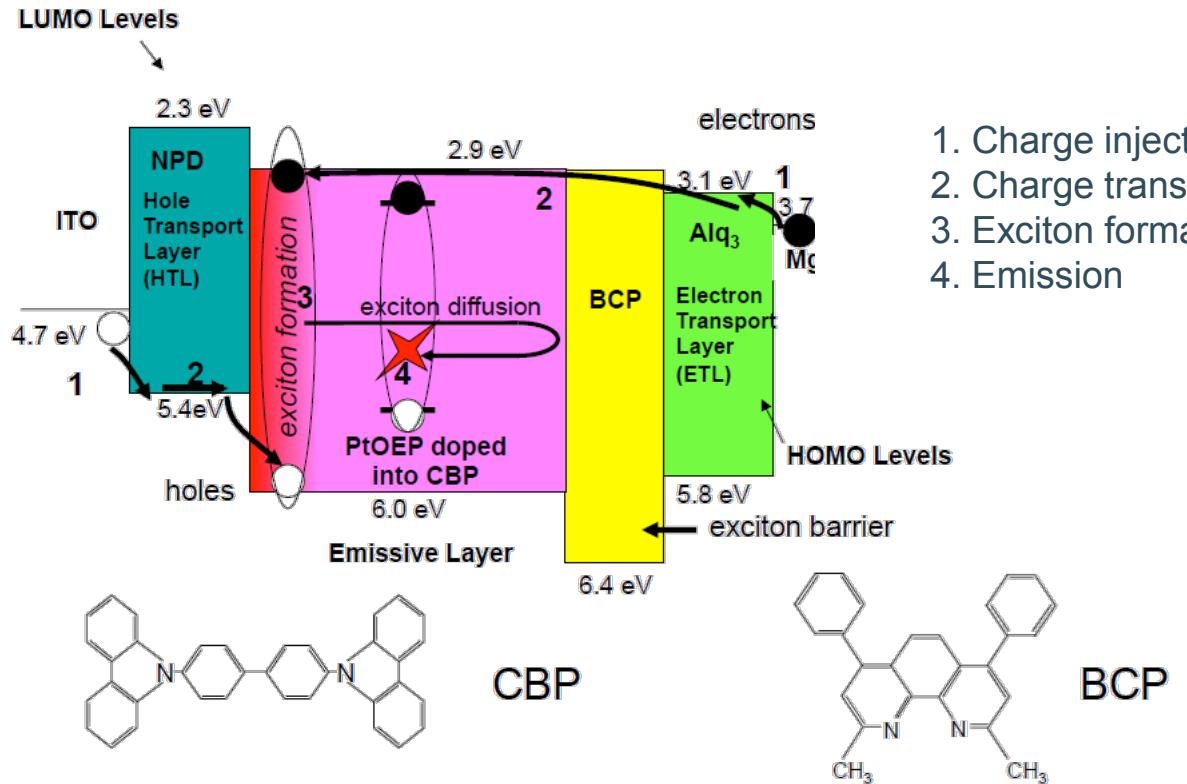
$$PCE = \frac{\text{Electrical power generated}}{\text{Incident optical power}} = \frac{P_{max}}{P_{in}}$$



DOI: [10.13140/RG.2.2.33851.67364](https://doi.org/10.13140/RG.2.2.33851.67364)

# Applications of organic electronic materials

- Organic light emitting diodes (OLEDs)
  - The most successful case of organic electronics



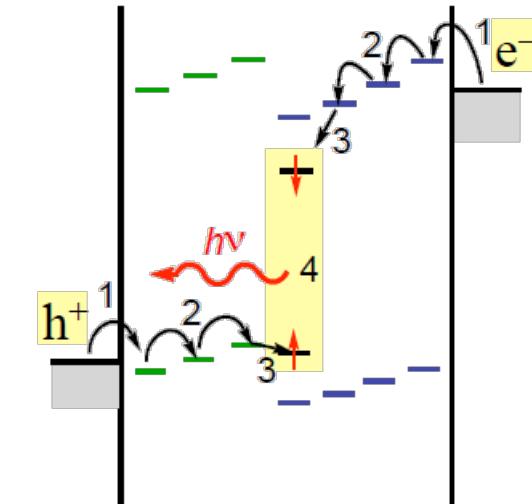
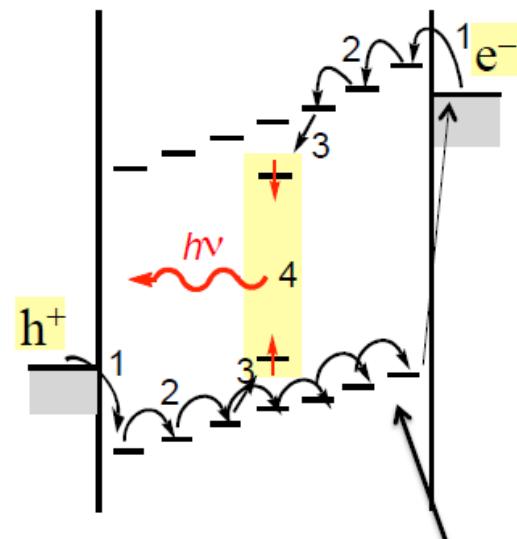
1. Charge injection
2. Charge transport
3. Exciton formation and diffusion
4. Emission



# Applications of organic electronic materials

- Organic light emitting diodes (OLEDs)
  - Structure: Multilayer

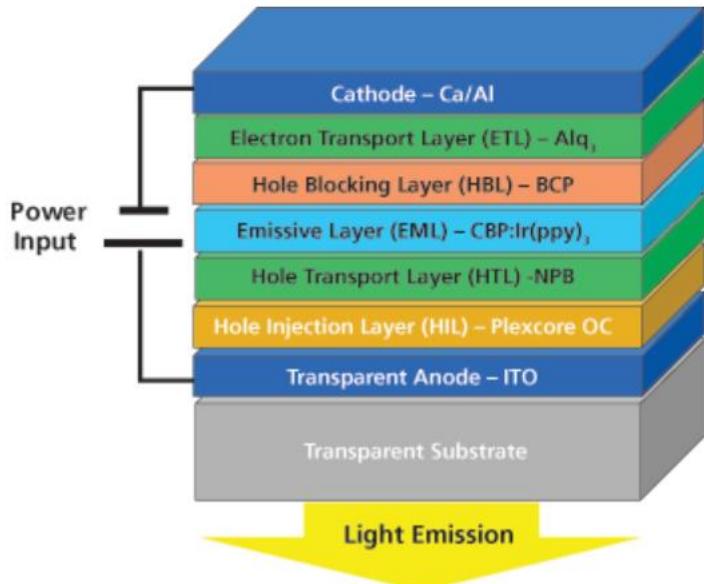
Multimaterial allows tuning charge transport balance



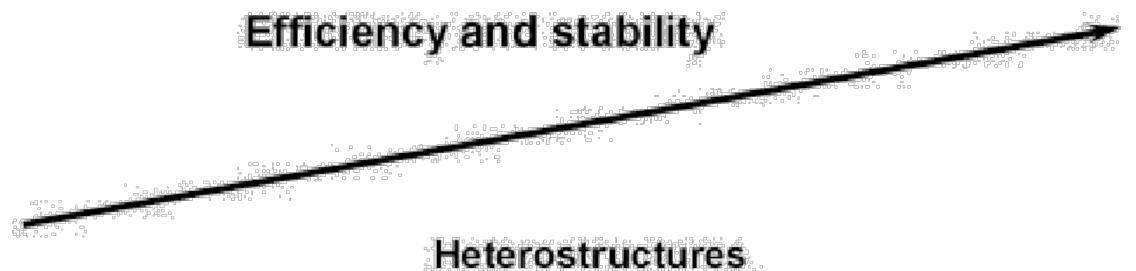
One layer makes it difficult to have balanced charge transport needed for high efficiency, specially considering the different mobility of  $h^+$  and  $e^-$

# Applications of organic electronic materials

- Organic light emitting diodes (OLEDs)
  - Structure: Multilayer



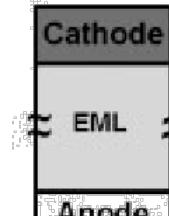
<https://www.sigmaaldrich.com/technical-documents/articles/materials-science/organic-electronics/plexcore-organic-conductive-inks.html>



Thick crystals

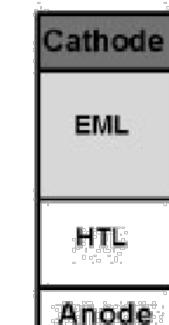
Pope (1963)  
Helfrich (1965)

Monolayer



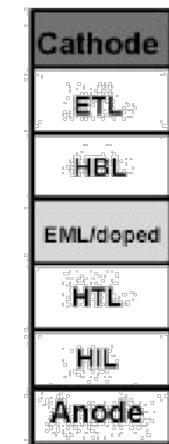
1965

2-layers

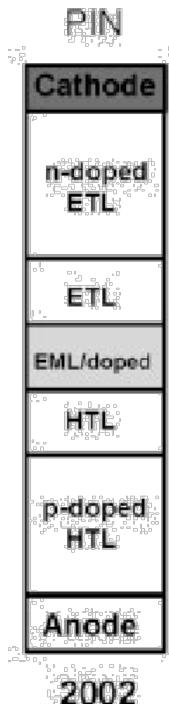


1985

Multilayers



DOI:10.1002/PI.1974

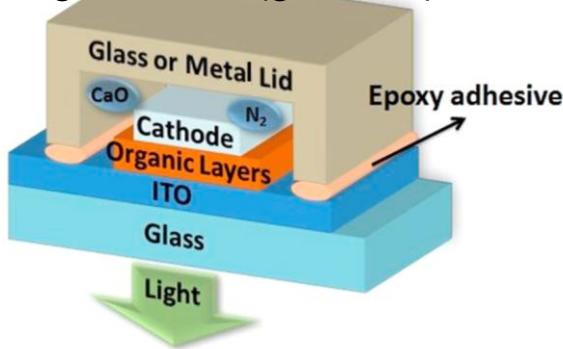


2002

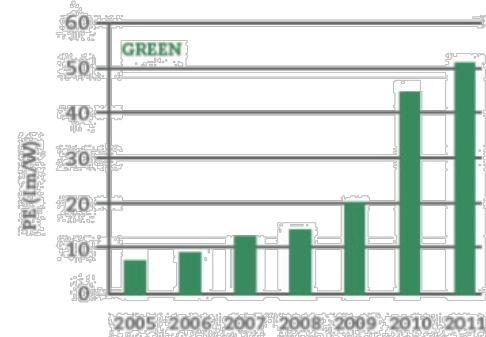
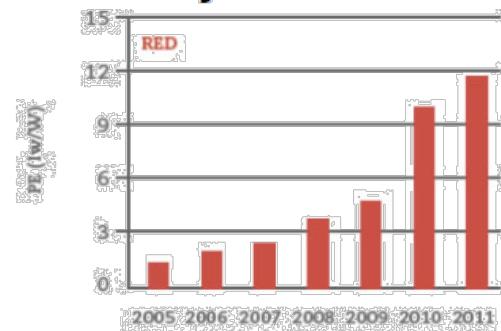
# Applications of organic electronic materials

- Organic light emitting diodes (OLEDs)
  - Problem of stability solved though material design and encapsulation

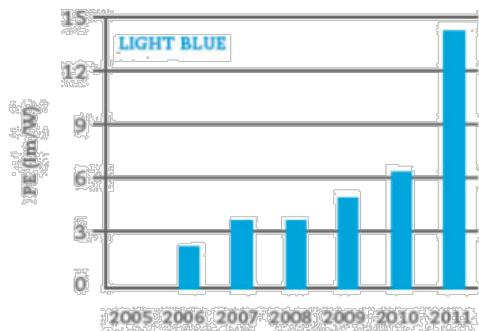
Encapsulation rigid device (glass lid)



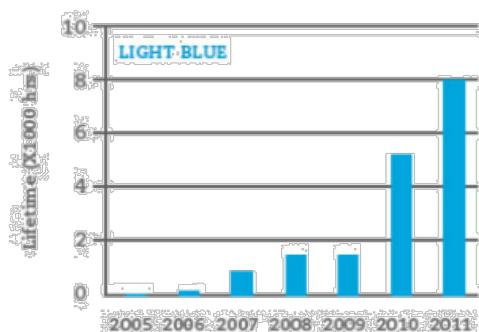
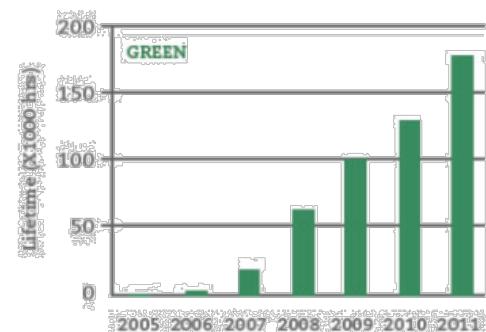
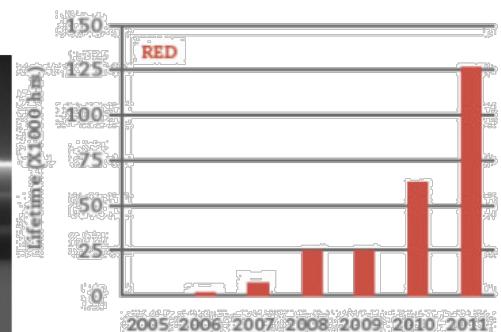
## Efficiency:



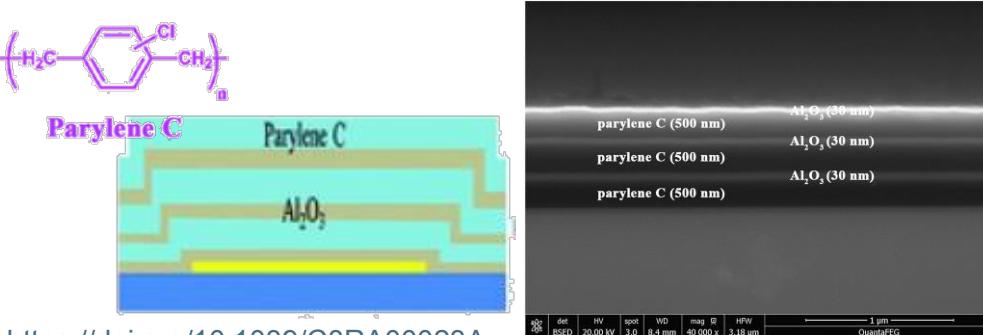
<https://www.oled-info.com/udc-pholed-material-performance-update-green-now-reaches-14-million-hours>



## Lifetime:



Encapsulation flexible device (multilayer think film)



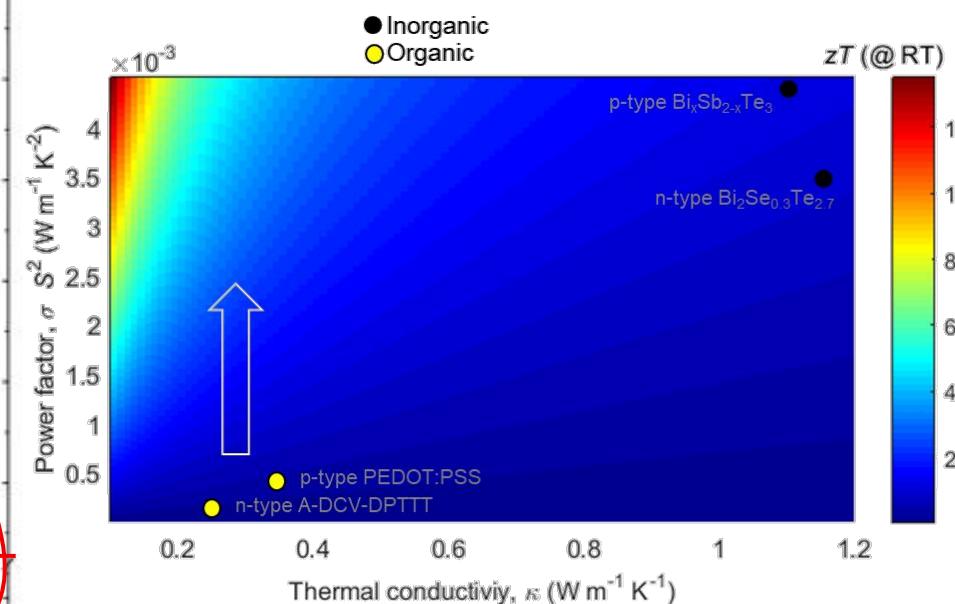
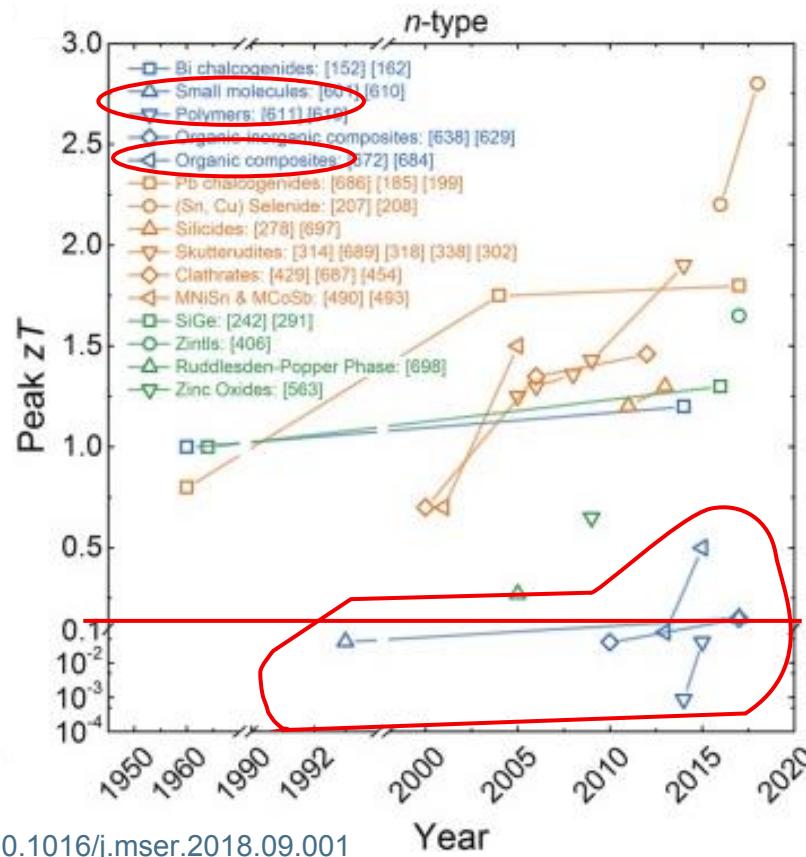
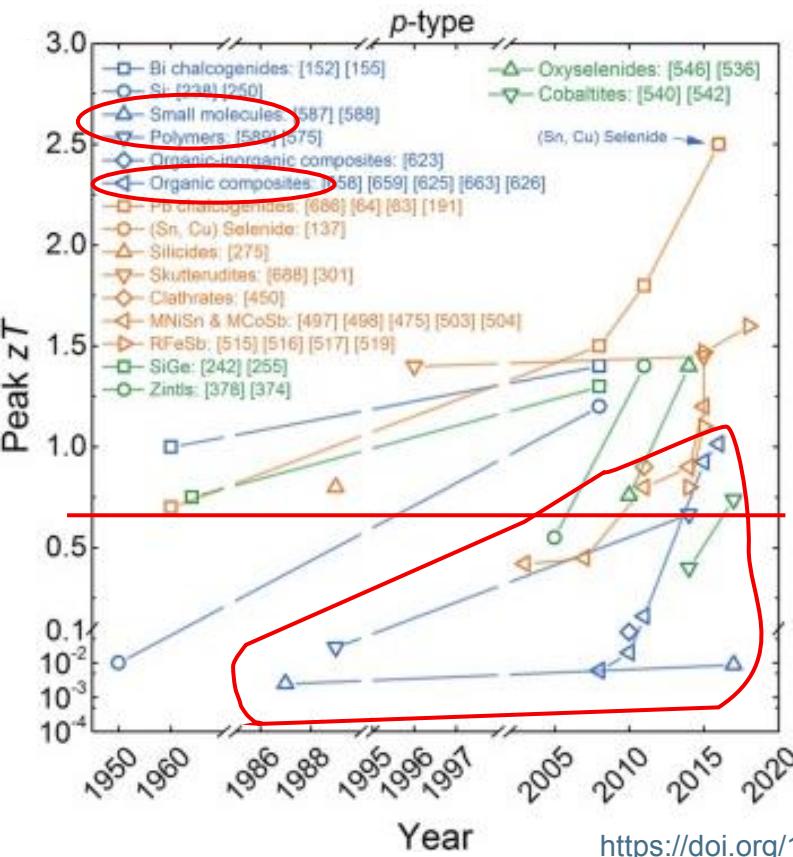
<https://doi.org/10.1039/C8RA00023A>

# Applications of organic electronic materials

- Organic light emitting diodes (OLEDs)
  - Why?
    - Compared to competing LCD technologies, OLEDs emit light and does not require backlight. It allows thinner devices.
    - Deep black is possible -> unparalleled  $10^6$  : 1 contrast because the device totally switches off. That permits also low power consumption (paramount for portable devices relying on a battery).
    - More vivid colors, better view at large angles.
    - AMOLED (active matrix organic LED) makes up 15% of mobile device displays in 2016 (LG, Samsung, etc.).

# Applications of organic electronic materials

- Organic thermoelectrics (OTEs): transform heat into electrical energy
  - Historical evolution



# Applications of organic electronic materials

- Organic thermoelectrics (OTEs):

- Efficiency:

Carnot efficiency

$$\eta = \frac{\Delta T}{T_{hot}} \frac{\sqrt{1 + zT_{avg}} - 1}{\sqrt{1 + zT_{avg}} + \frac{T_{cold}}{T_{hot}}} ;$$

- Figure of merit

Power factor

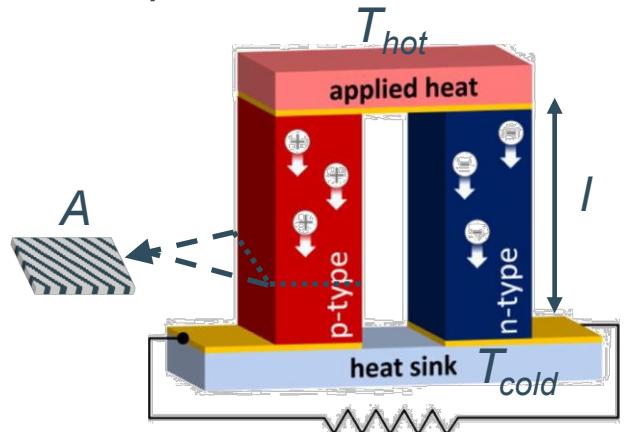
$$zT = \frac{S^2 \sigma T}{\kappa} ;$$

$S$  = Seebeck coefficient [ $\mu\text{V K}^{-1}$ ];

$\sigma$  = Electrical conductivity [ $\text{S cm}^{-1}$ ];

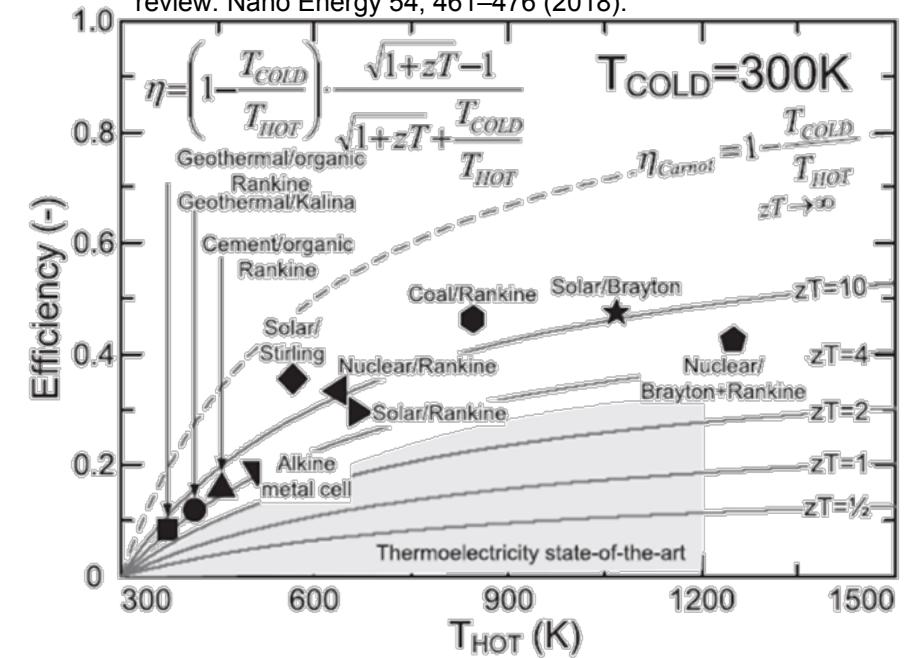
$\kappa = \kappa^{el} + \kappa^{ph}$  = thermal conduct. [ $\text{W m}^{-1} \text{K}^{-1}$ ];

$T$  = absolute temperature [K]



L. Cowen et al., ECS Journal of Solid State Science and Technology, 6 (3), 2017

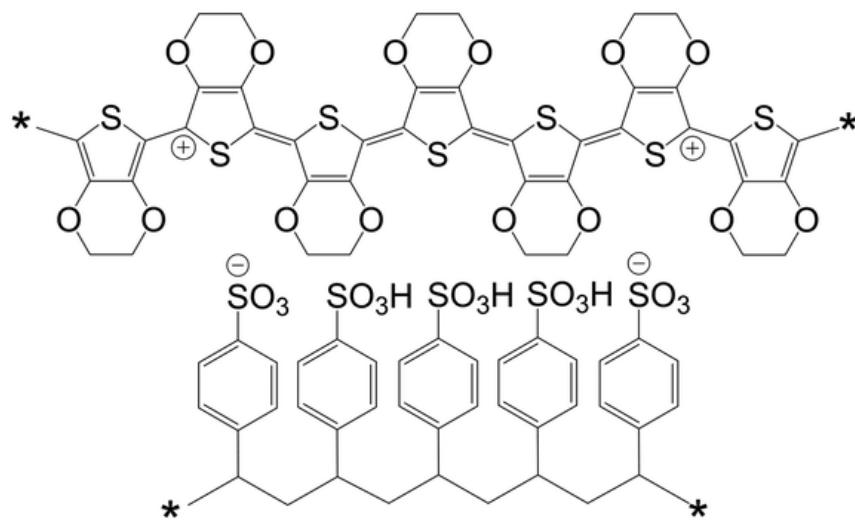
Haras, M. & Skotnicki, T. Thermoelectricity for IoT – A review. Nano Energy 54, 461–476 (2018).



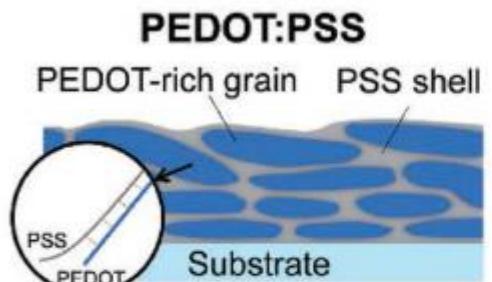
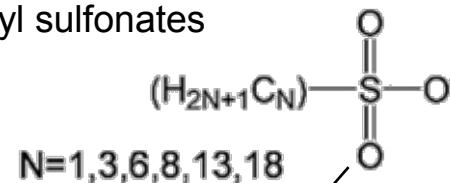
# Applications of organic electronic materials

- Organic thermoelectrics (OTEs): PEDOT and the importance of doping
  - PEDOT-derived polymers are so far **the most performing (p-type) organic thermoelectric materials.** They are usually doped with PSS and treated with small polar molecules (secondary dopants, SD) to improve morphology and performance.

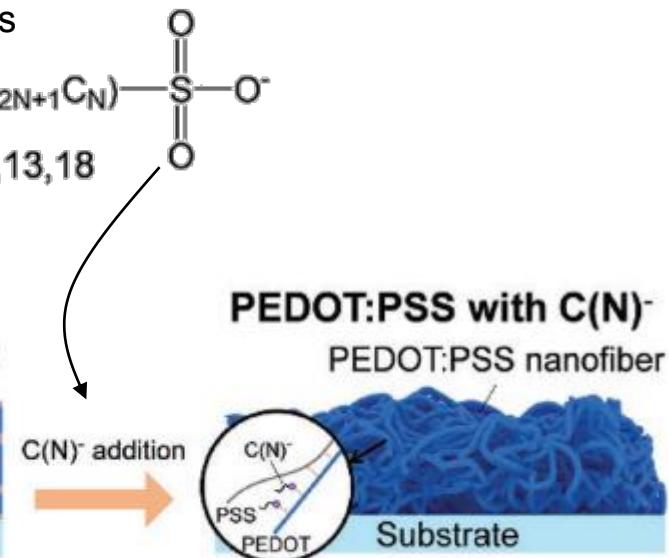
PEDOT:PSS



Sodium alkyl sulfonates



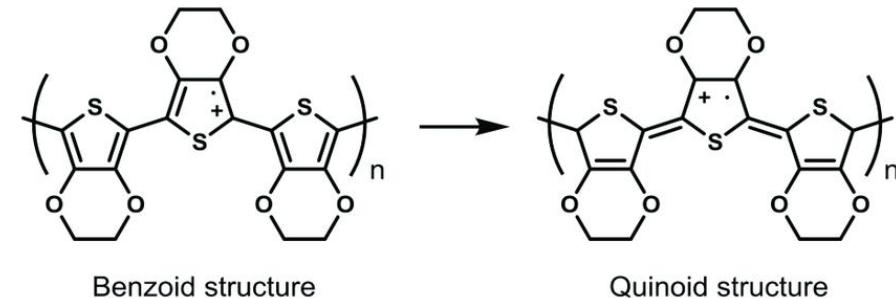
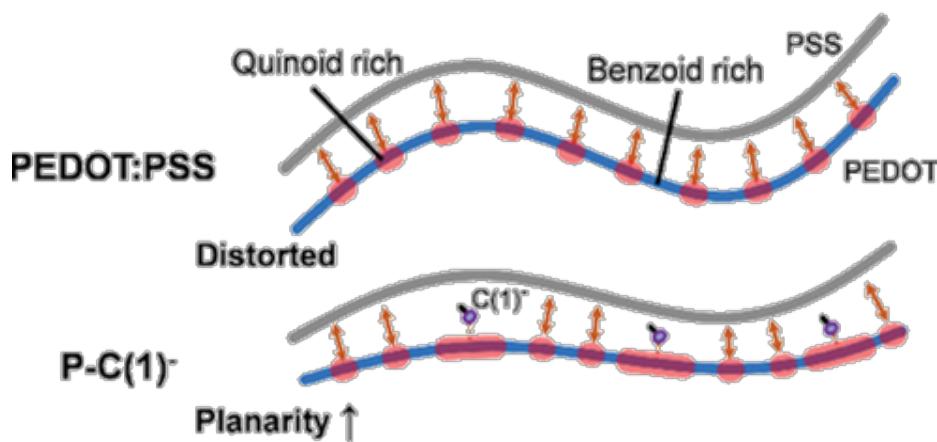
Pancake-like morphology



Nanofibrous morphology

# Applications of organic electronic materials

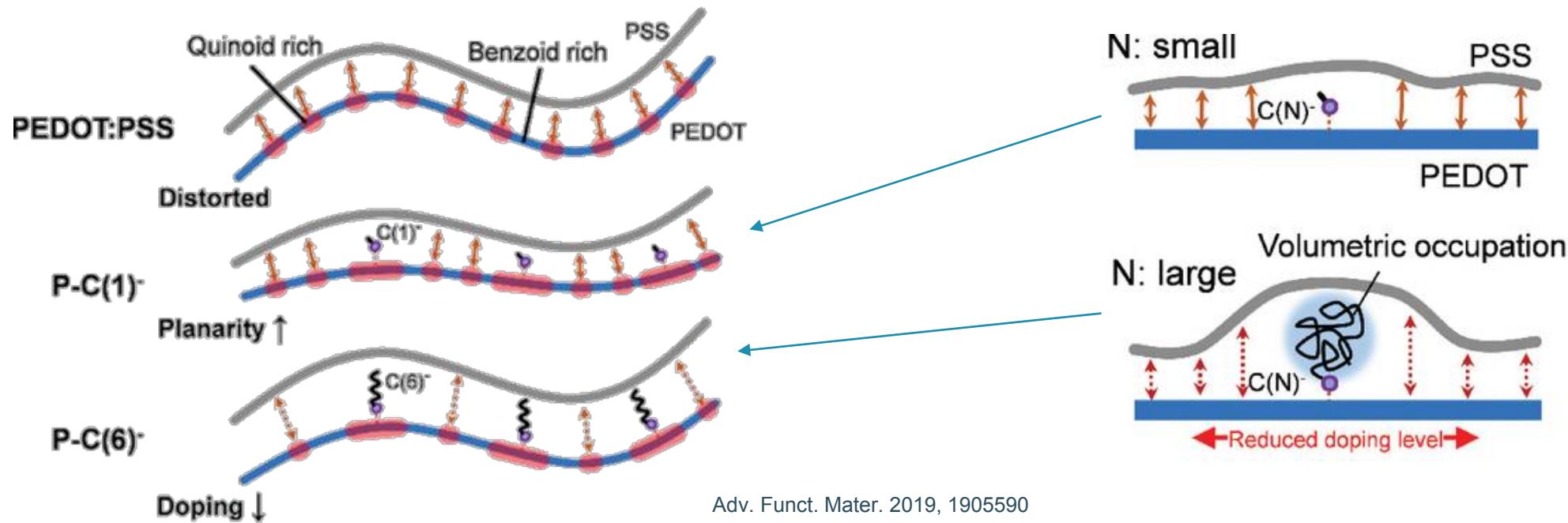
- Organic thermoelectrics (OTEs): PEDOT and the importance of doping
  - Effect of the SD on morphology and transport: SD compete with PSS for the binding sites. If the SD molecule is small, it will induce more quinoid segments in the PEDOT chains than PSS without significant dedoping.
  - Quinoid segments are more rigid and planar, promoting better  $\pi$ - $\pi$  stacking. This can be observed in GIWAXS (see next slides).



Funct. Mater. 2019, 1905590

# Applications of organic electronic materials

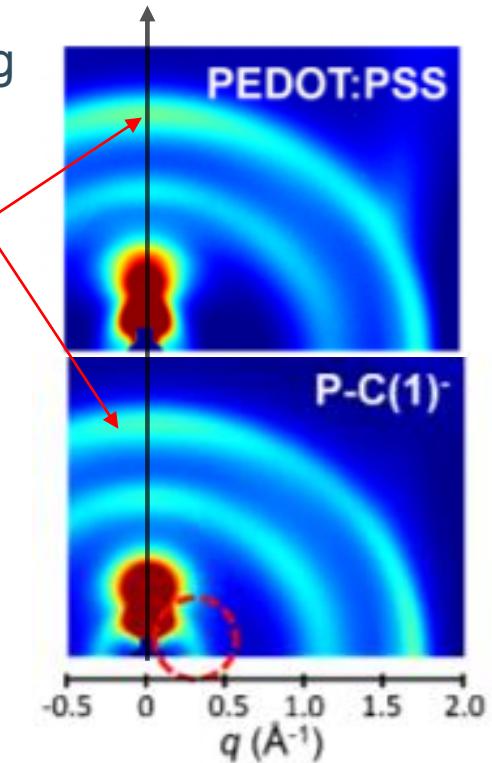
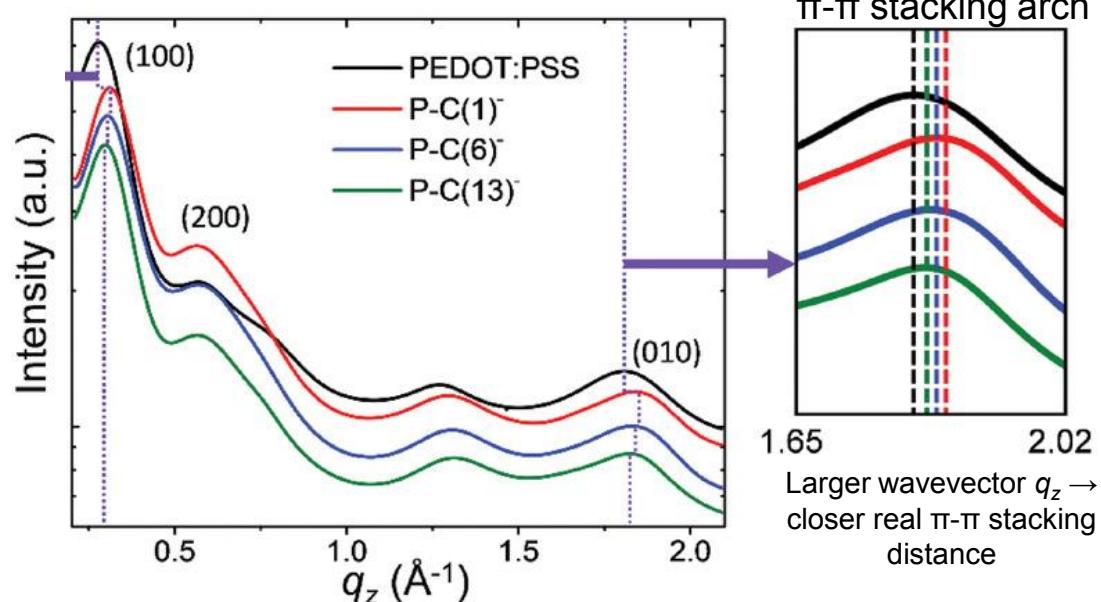
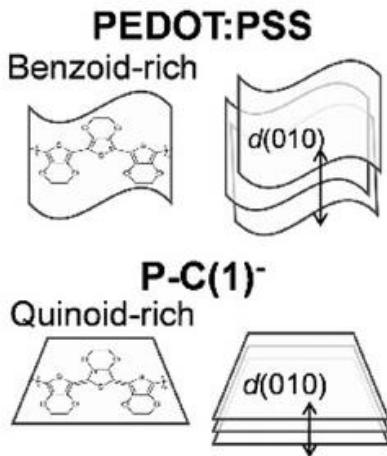
- Organic thermoelectrics (OTEs): PEDOT and the importance of doping
  - Effect of the SC on morphology and transport: On the other hand, if the SD is a large molecule (large volumetric occupation), it will separate a large segment of PSS away from PEDOT, producing dedoping and a reduction of quinoid segments (less planar molecule).



# Applications of organic electronic materials

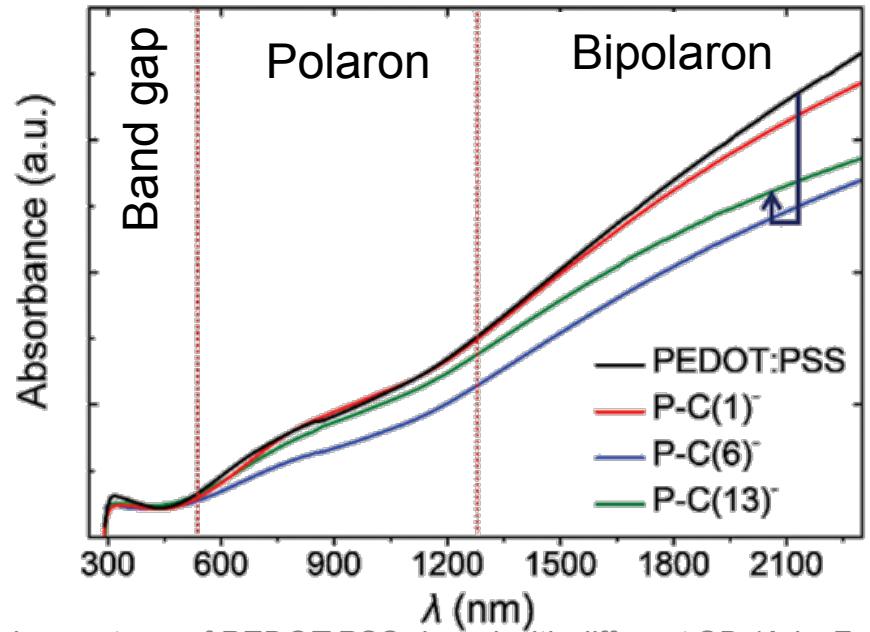
- Organic thermoelectrics (OTEs): PEDOT and the importance of doping

- Effect of the SC on morphology and transport : Quinoid segments are more rigid and planar, promoting better  $\pi$ - $\pi$  stacking. This translates in a shorter  $\pi$ - $\pi$  stacking distance that is beneficial for charge carrier transport for PEDOT:PSS doped with small molecules. The  $\pi$ - $\pi$  stacking distance can be observed in GIWAXS.



# Applications of organic electronic materials

- Organic thermoelectrics (OTEs): PEDOT and the importance of doping



UV-vis spectrum of PEDOT:PSS doped with different SD (Adv. Funct. Mater. 2019, 1905590).

- Effect of the SC on morphology and transport :  
Despite modifying the morphology, small SD do not change the oxidation level of PEDOT:PSS significantly, i.e. no dedoping is observed for C(1)<sup>-</sup>. Larger SD molecules such as C(6)<sup>-</sup> and C(13)<sup>-</sup> are more efficient for dedoping.

# Applications of organic electronic materials

- Organic thermoelectrics (OTEs): PEDOT and the importance of doping
  - Effect of the SC on morphology and transport : The effect of morphology and doping can be seen in TE performances.
  - Remember from Chapter 3 & 7 that:

$$\sigma = qn\mu,$$

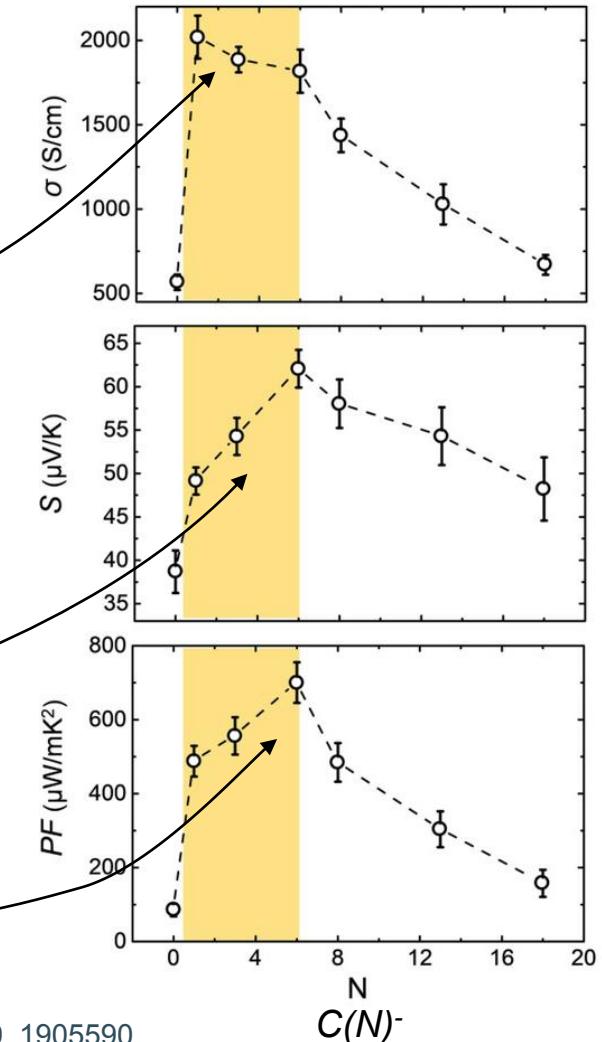
$\sigma$  increases owing to a higher  $\mu$  resulting from molecular arrangement when using C(1)- C(6)-. As larger SD molecules are used, there is a dedoping effect, which decreases  $n$  but the increase of  $\mu$  is still more relevant.

$$S = \frac{8\pi^2 k_B^2}{3qh^2} m^* T \left(\frac{\pi}{3n}\right)^{2/3}$$

The dedoping effect, very visible for C(6)-, results in lower  $n$  and a higher Seebeck coefficient.

$$PF = \sigma S^2$$

There is a “sweet spot” where the power factor gets a maximum.



Adv. Funct. Mater. 2019, 1905590



# Based on the previous example, how would you increase the conductivity to improve the PF of OTEs, by doping or by tuning the molecular arrangement?

By doping

by tuning the molecular arrangement

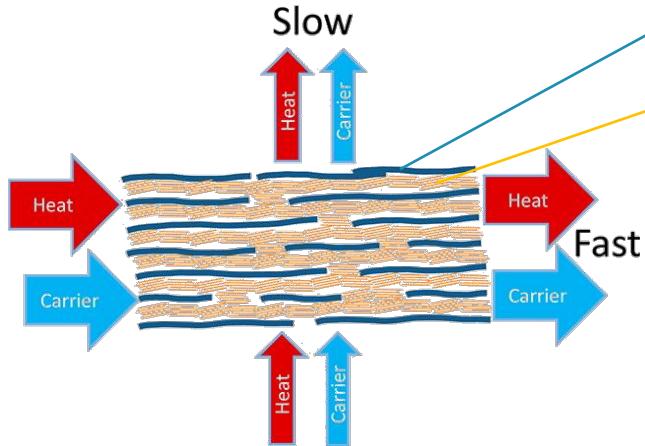
Both would work

Neither

# Applications of organic electronic materials

- Organic thermoelectrics (OTEs): Importance of morphology
  - Chain orientation and crystallinity

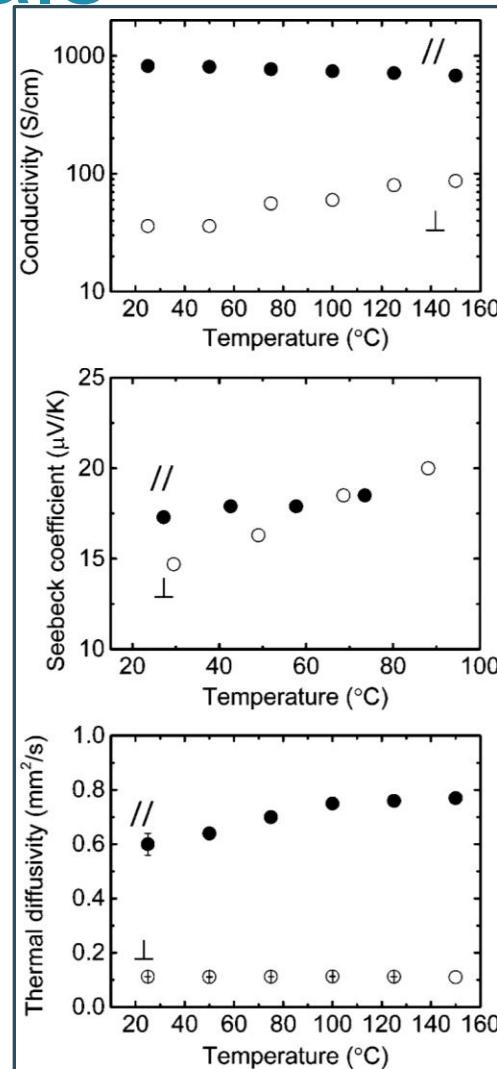
Sketch showing the directions of preferential and non-preferential transport in PEDOT:PSS. The blue and yellow lines represent PEDOT chains (oriented in plane) and PSS, respectively.



TE parameters vs temperature measured in plane (II) and through plane (L) (note that thermal diffusivity and thermal conductivity,  $\kappa$ , are linearly related by the equation  $\kappa = \text{density} \times \text{specific heat capacity} \times \text{diffusivity}$ ).

The electrical conductivity is enhanced more than the thermal conductivity along the molecule backbone.  $S$  does not change much. Therefore **alignment seems beneficial for  $zT$ !**

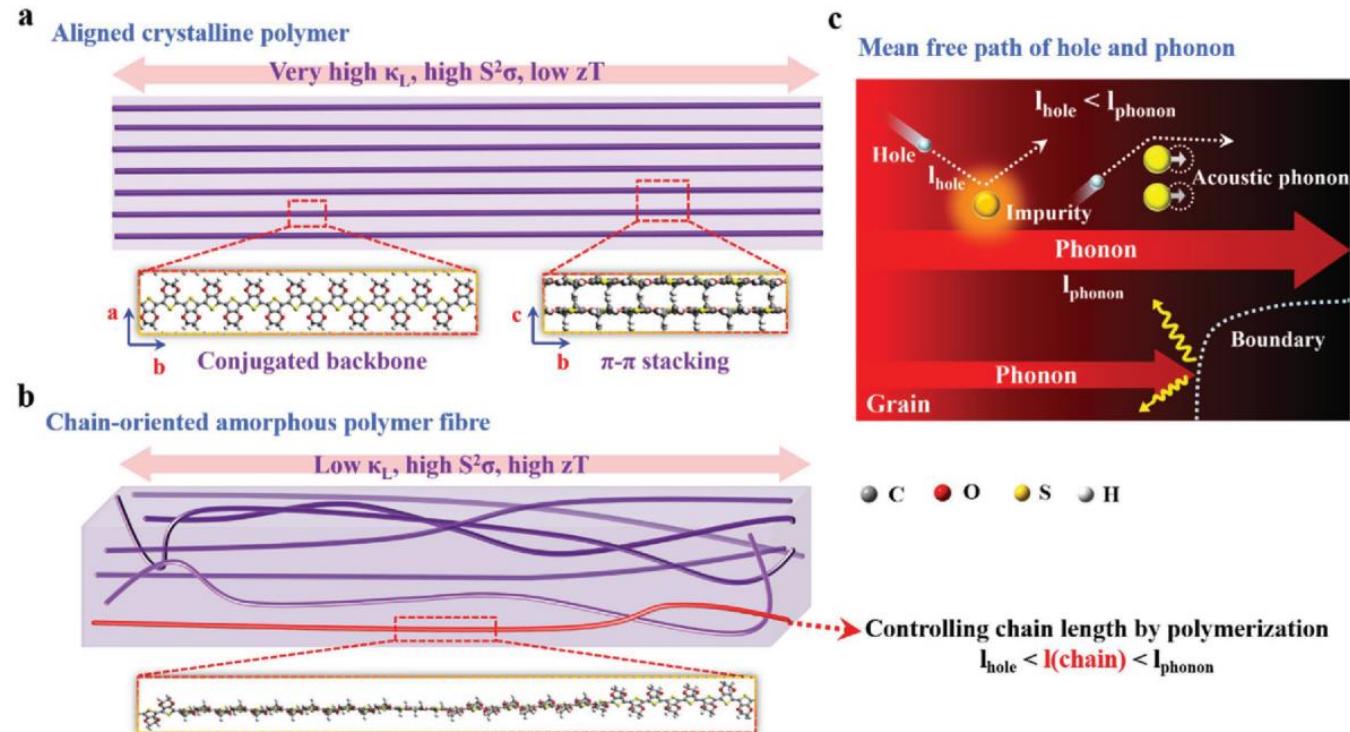
[dx.doi.org/10.1021/mz500446z](https://dx.doi.org/10.1021/mz500446z) |



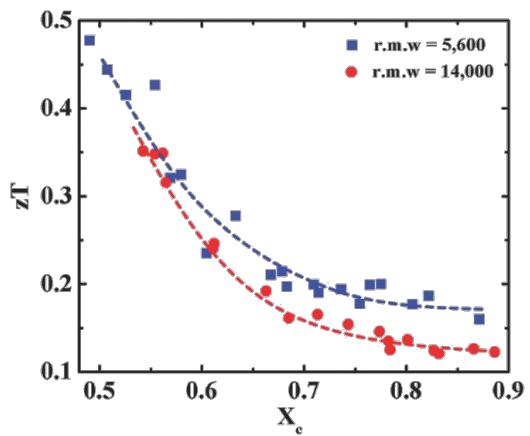
# Applications of organic electronic materials

- Organic thermoelectrics (OTEs): Importance of morphology
  - Chain orientation and crystallinity

Simulated figure of merit,  $zT$ , versus crystallinity,  $X_c$ , for uniaxial-aligned PEDOT fibres with two different values of molecular weight. High crystallinity is not desirable since it leads to a high  $\kappa$ .



DOI: 10.1002/adfm.201702847

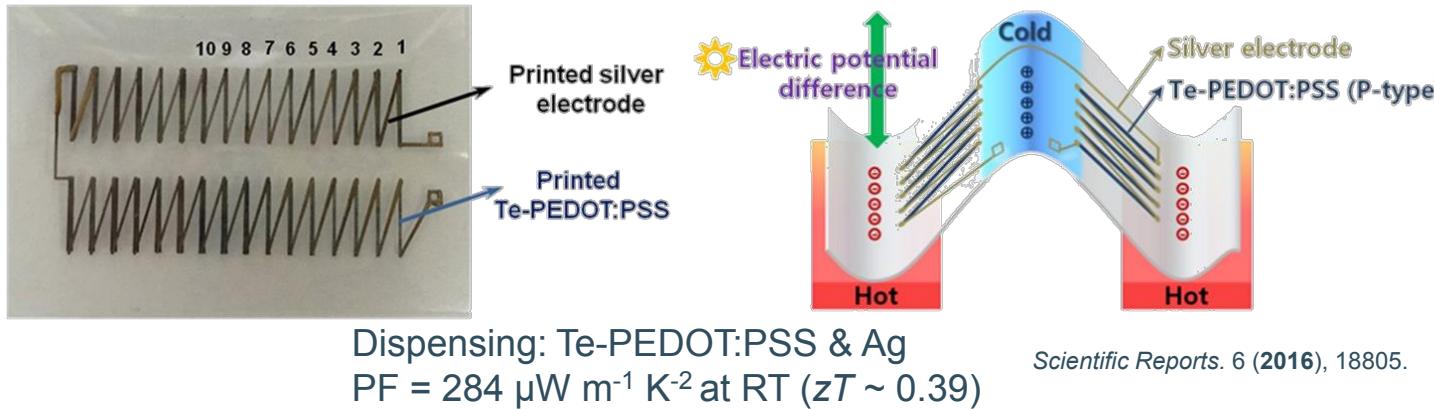


Graphical representation of the effect of uniaxial alignment and crystallinity in the transport and sketch representing the typical scattering events for phonons and charge carriers in a crystallite.

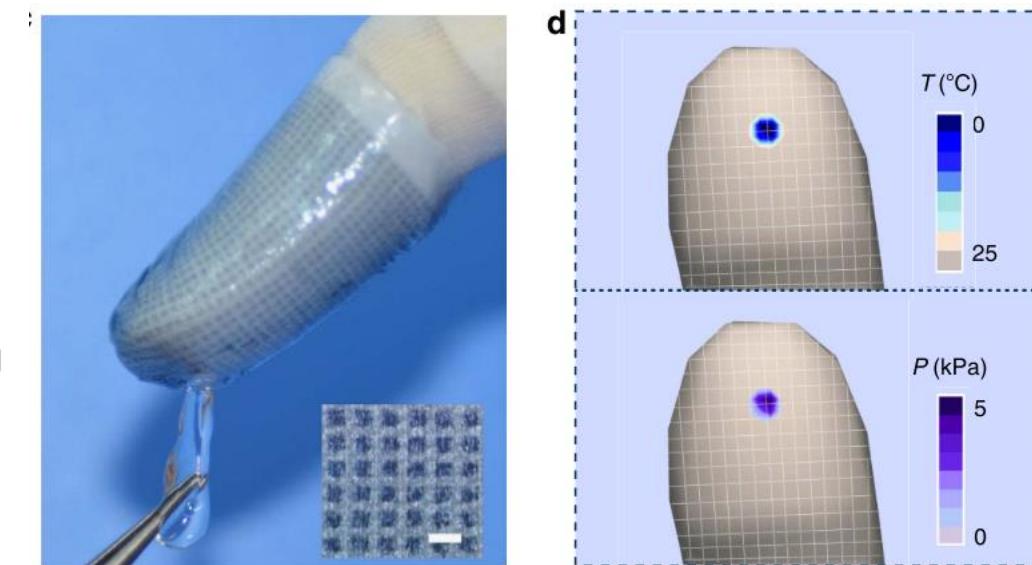
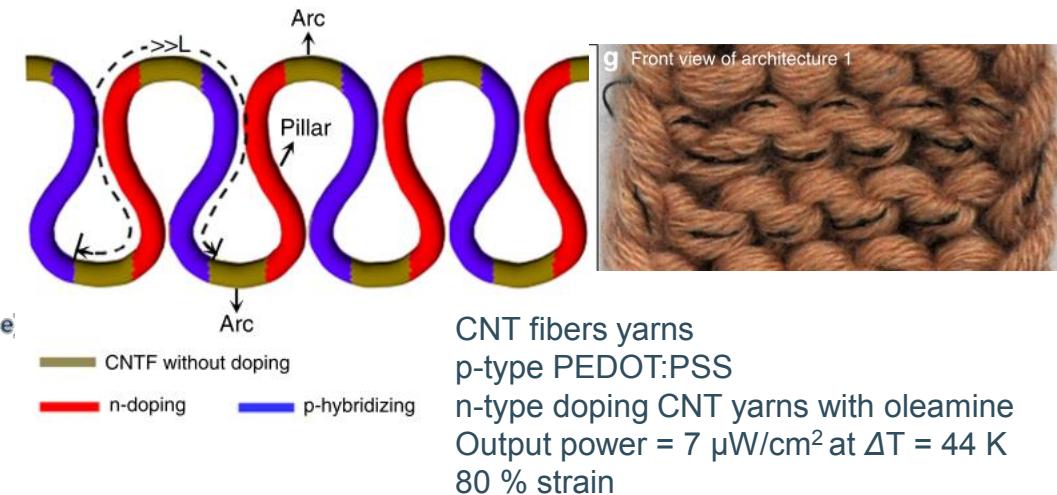
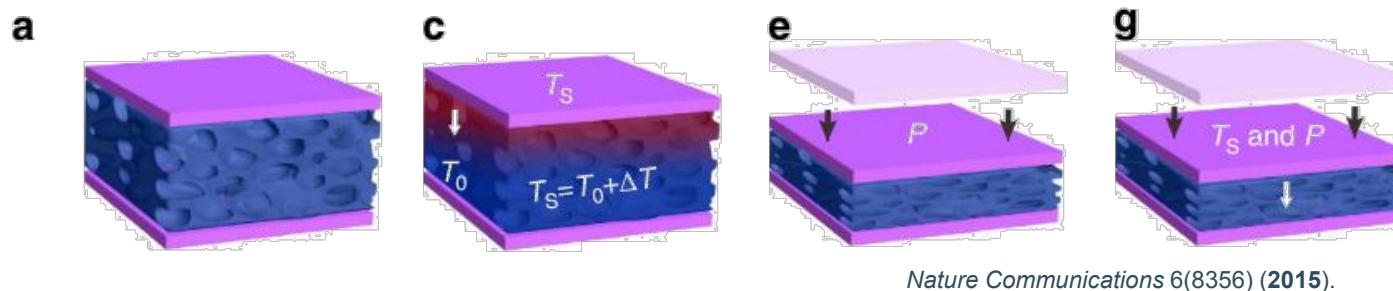
The mean free path (MFP) of phonons is longer than that of charge carriers. Therefore, by tailoring the length of the oriented molecules (or the size of the crystallites) to be longer than the charge carriers MFP but shorter than the phonons MFP, higher boundary scattering will occur for phonons. Thus, thermal transport will be suppressed more efficiently than charge carrier transport.

# Applications of organic electronic materials

- Organic thermoelectrics (OTEs): Applications
  - Printed and flexible energy harvesters



- Flexible self-powered sensors for e-skin: PEDOT:PSS TE used as dual (temp and pressure) sensor.



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- Mentioned references
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# Materials Physics and Technology for Nanoelectronics

KU LEUVEN

imec

KU LEUVEN

MATERIAALKUNDE

**Clement Merckling**

clement.merckling@imec.be

IMEC IV, room 2.36

Kapeldreef 75, B-3001 Leuven

**Francisco Molina-Lopez**

francisco.molinalopez@kuleuven.be

Dept. Materials Engineering, room 01.51

Kasteelpark Arenberg 44, B-3001 Leuven