Organic light-emitting diodes

Charge injection and transport

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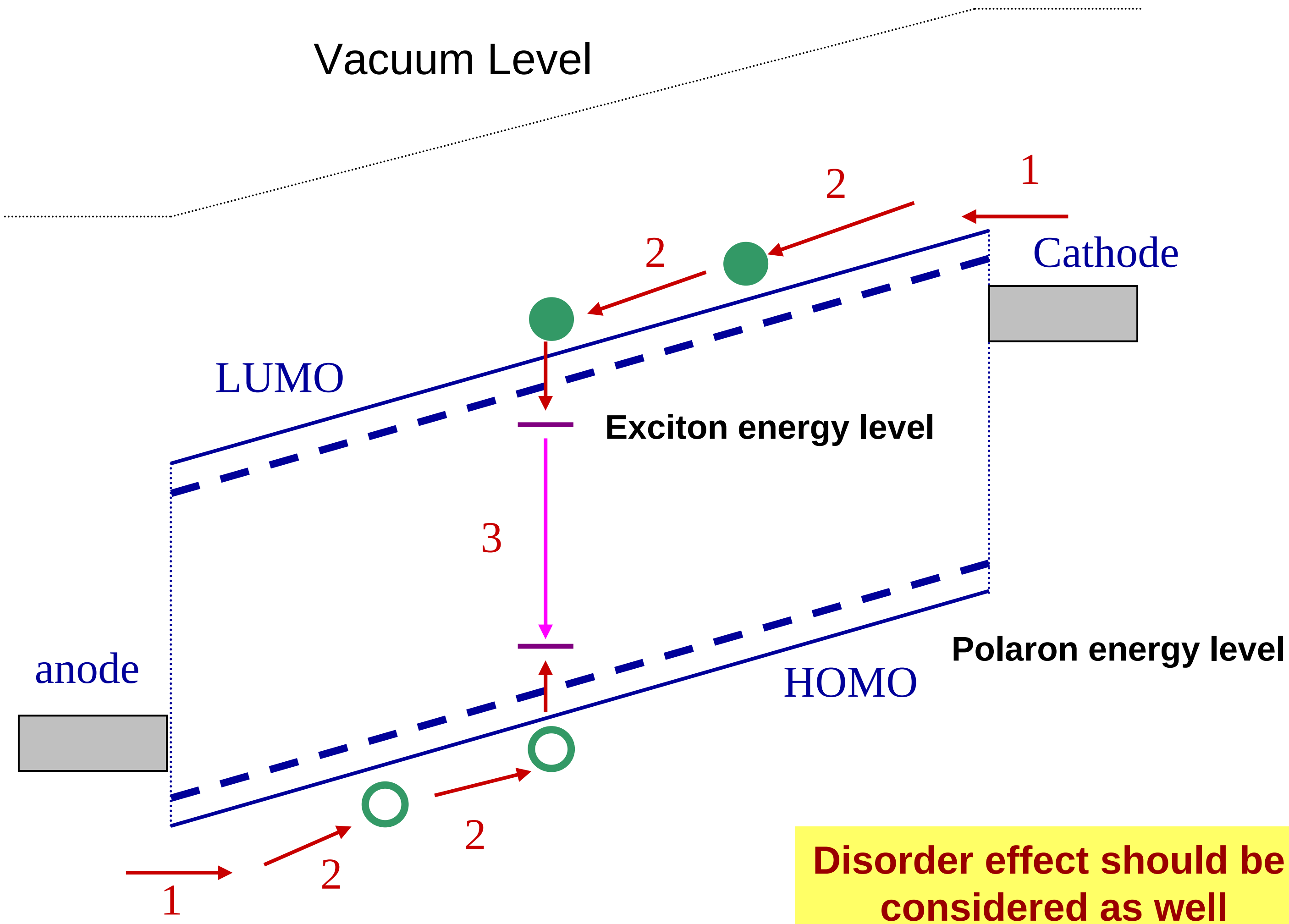
Closer look at the electric processes in OLEDs



Disorder effect should be considered as well

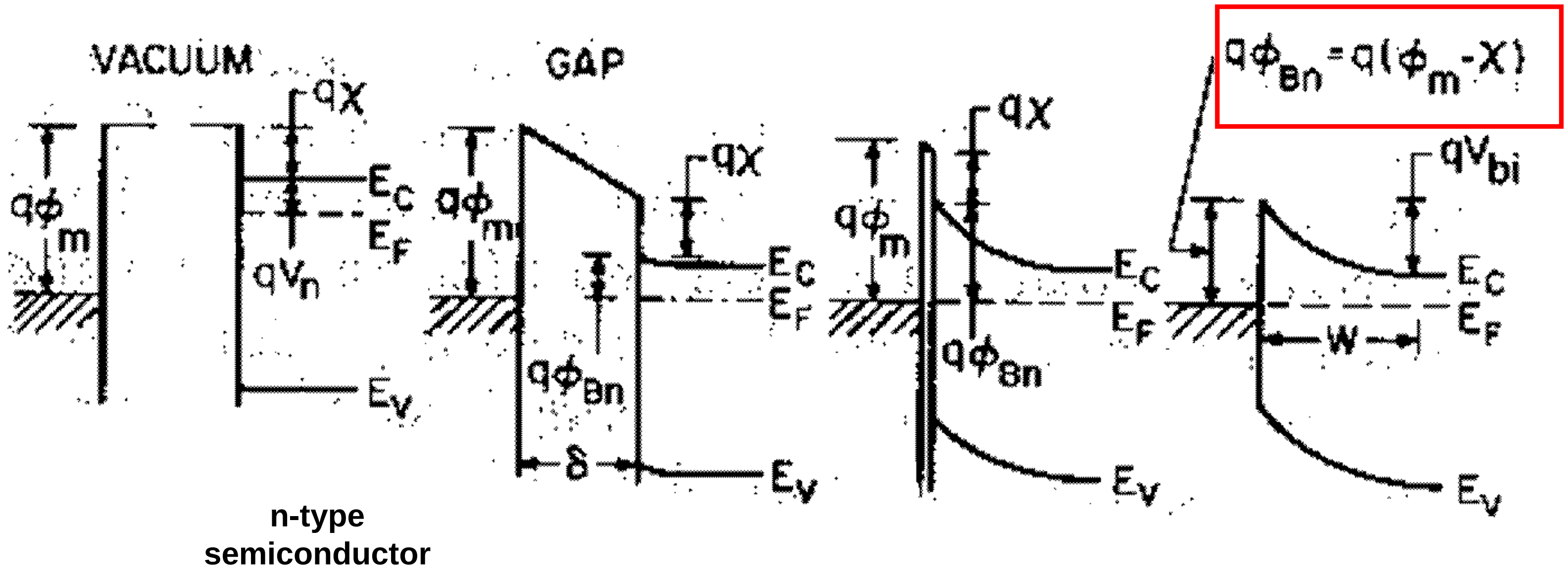
Ohmic Contact

A metal-semiconductor contact that has negligible contact resistance relative to the bulk or spreading resistance of the semiconductor

A satisfactory ohmic contact should not significantly perturb device performance

The ohmic contact has no rectification

Metal-Semiconductor Contact



Work function: $q\Phi_m$ (metal) $q(\chi+V_n)$ (semiconductor)

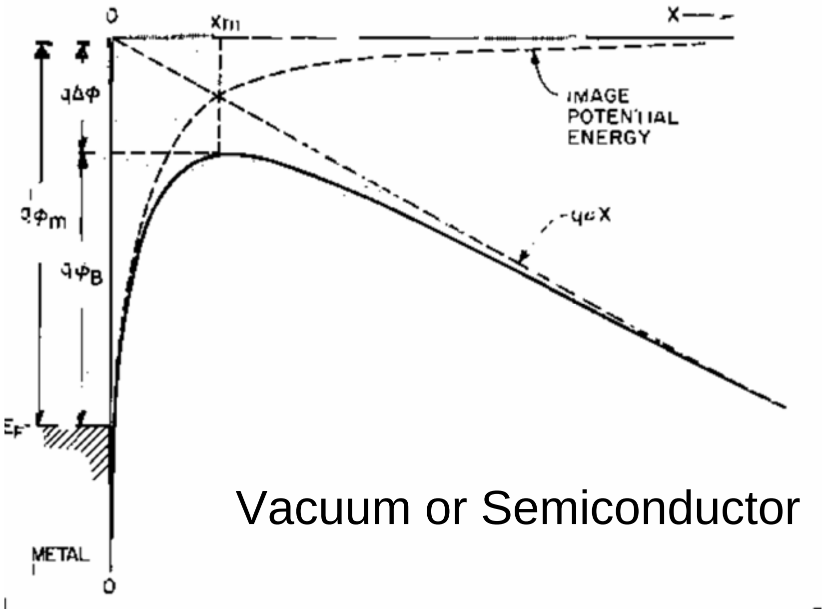
V_n: the energy different between E_C and E_F

Depletion depth : $$W = \left(\frac{2\varepsilon_S(V_{bi}+V_R)}{eN_d}\right)^{1/2}$$

S. M. Sze, Physics of Semiconductor Devices (Wiley, New York, 1981)

Schottky Effect

The image-force-induced lowing of the potential energy for charge carrier emission when an electric field is applied



$$\Delta\Phi = \left(\frac{eE}{4\pi\varepsilon_s}\right)^{1/2}$$

S. M. Sze, Physics of Semiconductor Devices (Wiley, New York, 1981)

The current transport process

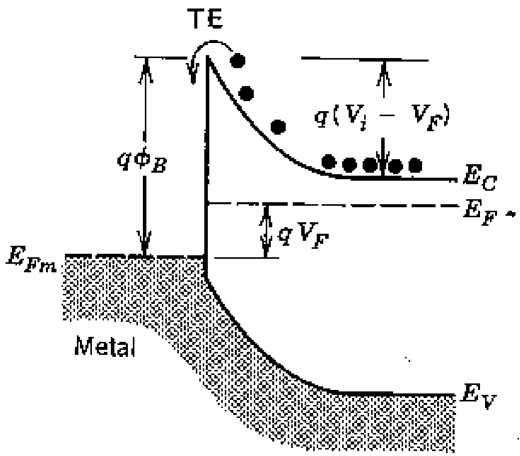
Thermionic Emission is the dominant mechanism

$$j_{RS} = A^* T^2 \exp\left(- \frac{\Phi_B - \beta_{RS}\sqrt{F}}{k_B T} \right)$$

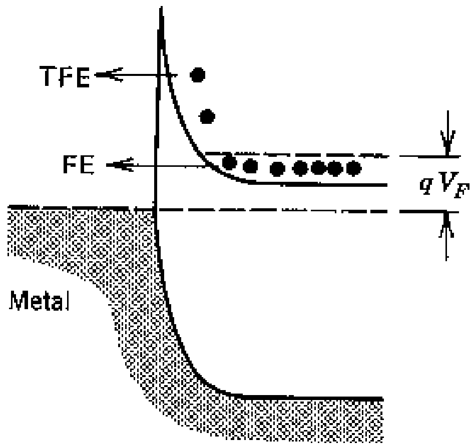
Richardson constant $A^* = 4\pi q m^* k_B^2 / h^3$

$$\beta_{RS} = \sqrt{q^3 / 4\pi\varepsilon\varepsilon_0}$$

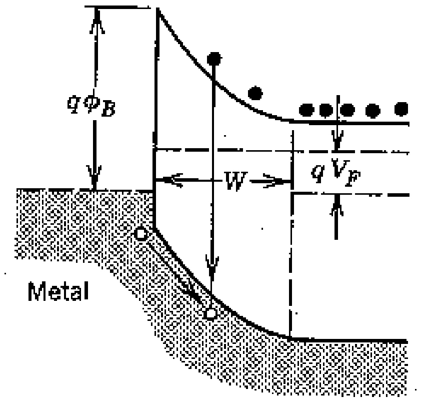
zero-field injection barrier Φ_B



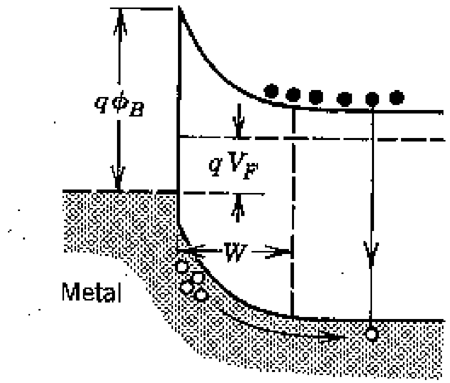
thermionic emission



tunneling



electron-hole
pair recombination

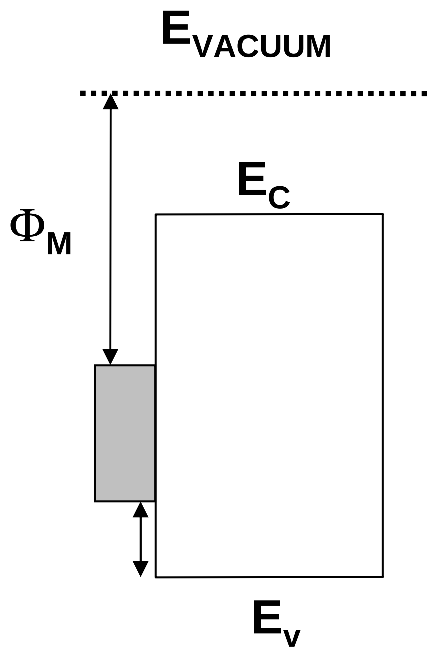


minority carrier injection

Organic/Metal interface

First approximation :
A "clean" organic and metal interface
In the absent of doping, interface dipoles and other effect,
The depletion depth (W) is much large than the layer thickness (t)

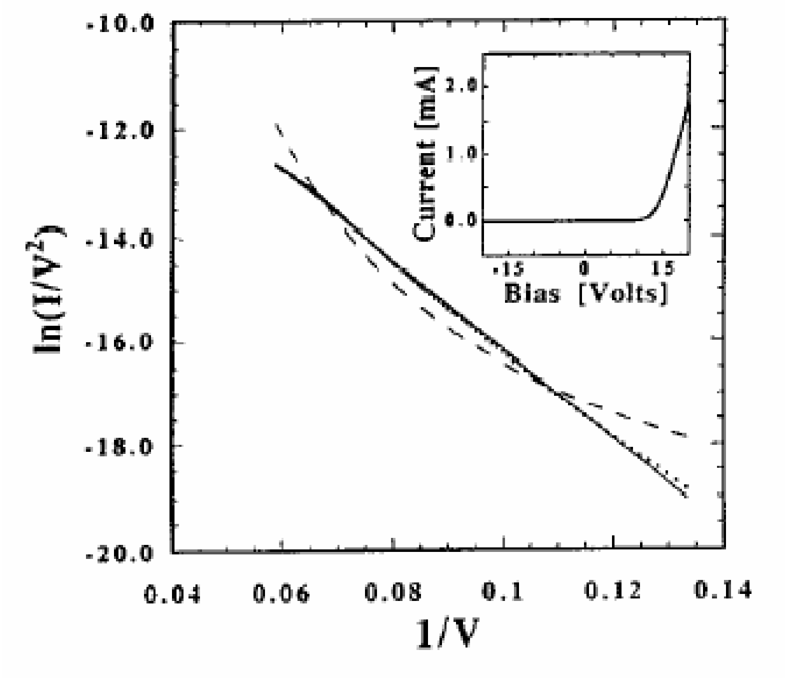
W >> t



Depletion depth : $W = \left(\dfrac{2\varepsilon_S (V_{bi} + V_R)}{eN_d} \right)^{1/2}$

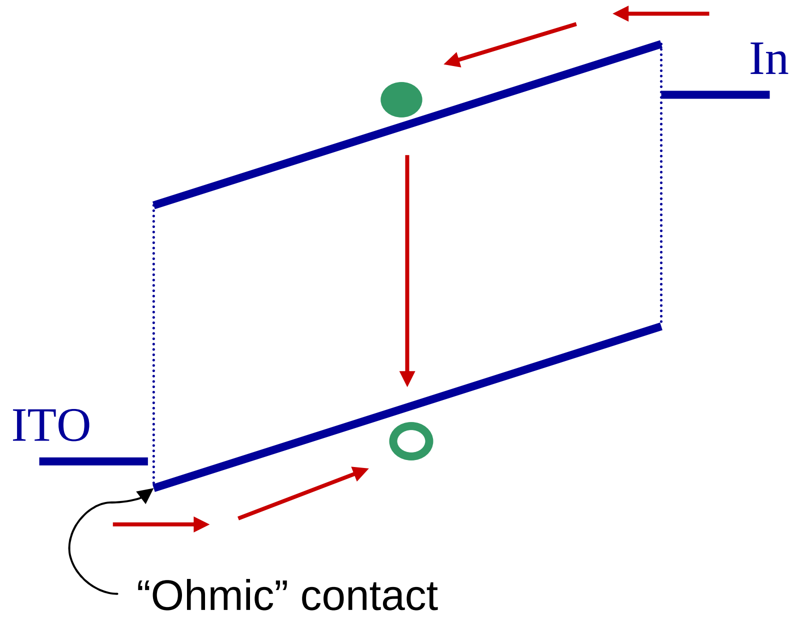
Thermionic emission vs Tunneling

In/MEH-PPV diode



Dashed line : thermionic emission
Solid line: tunneling

Oversimplied!!



Field dependence:

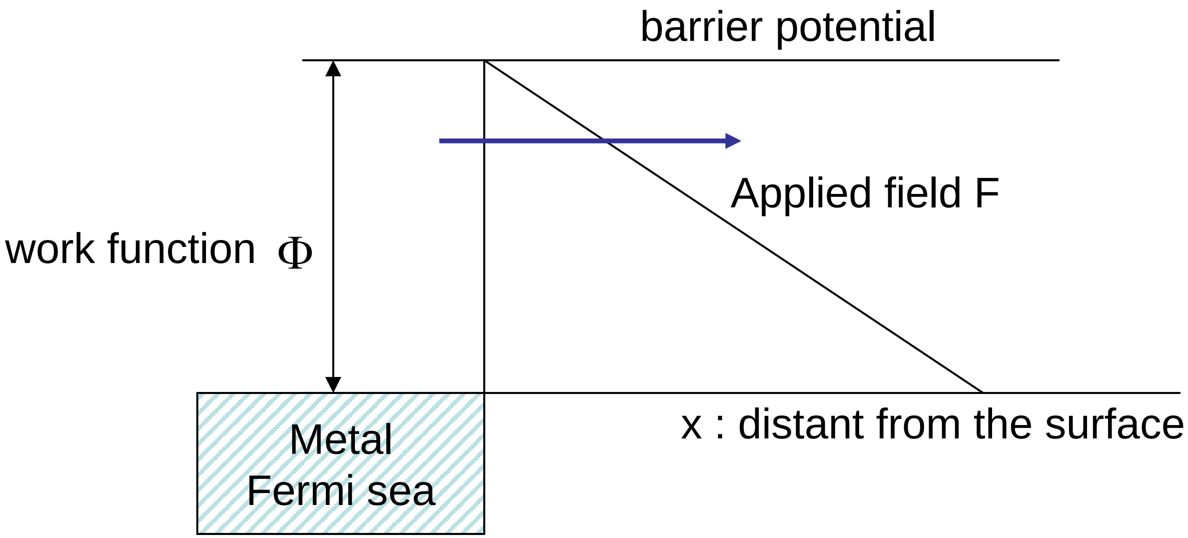
Thermionic emission: $I \propto \exp(-eV/nKT)$

Tunneling: $I \propto V^2 \exp(-b/V)$

D. Braun & A. J. Heeger, APL 58, 1982 (1991)

Tunneling

Quantum mechanism were first applied to the field emission of electrons from a metal by Fowler & Nordheim

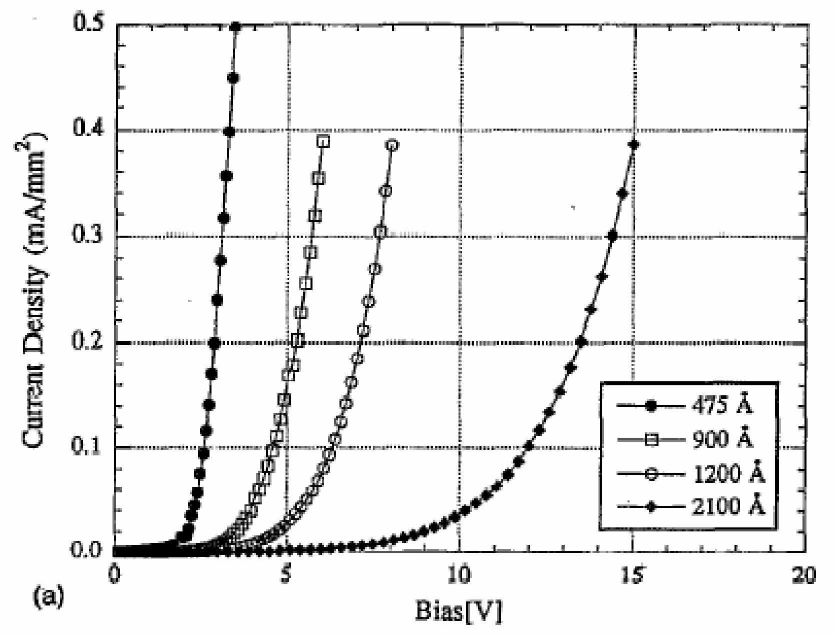


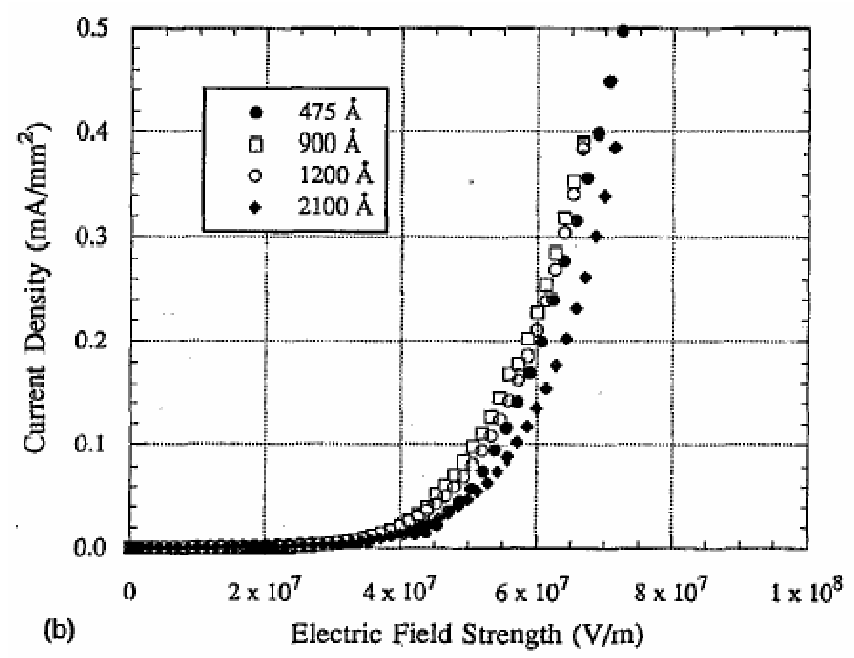
$$j_{\mathrm{FN}} = \frac{A^* q^2 F^2}{\Phi_{\mathrm{B}} \alpha^2 k_{\mathrm{B}}^2} \exp\left(-\frac{2\alpha \Phi_{\mathrm{B}}^{3/2}}{3qF} \right)$$

$$\text{with} \quad \alpha = \frac{4\pi\sqrt{2m^*}}{h}.$$

Thickness dependence of I-V characteristics

ITO/MEH-PPV/Ca





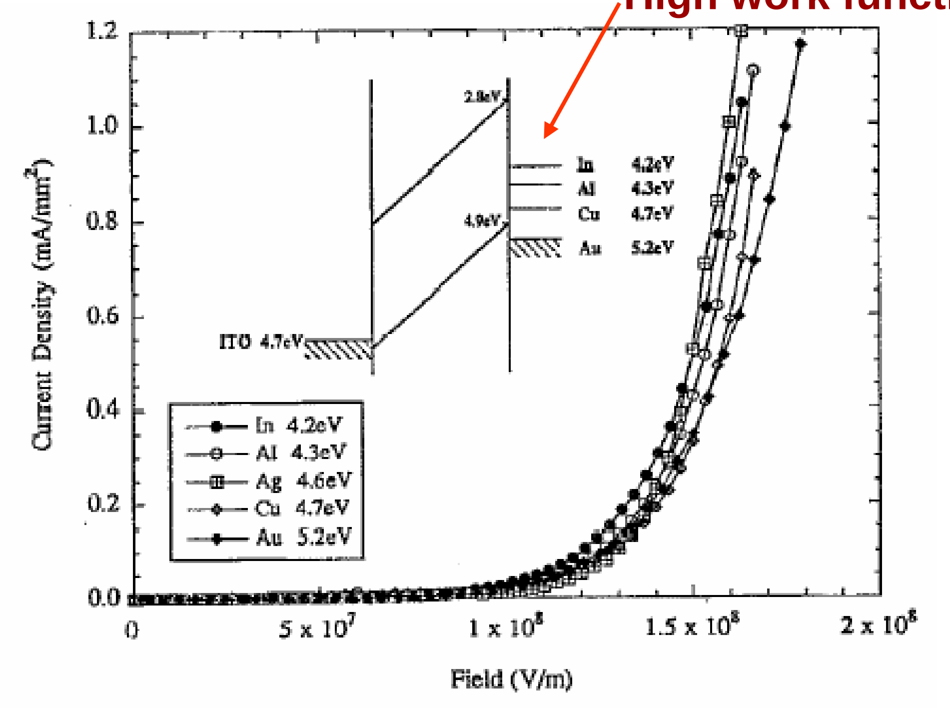
I-V characteristics depend, not on the voltage, but on the electric field

I. D. Parker JAP 75, 1656 (1994)

The very first systematic study of the charge injection

"Hole-only" device

High work function metals

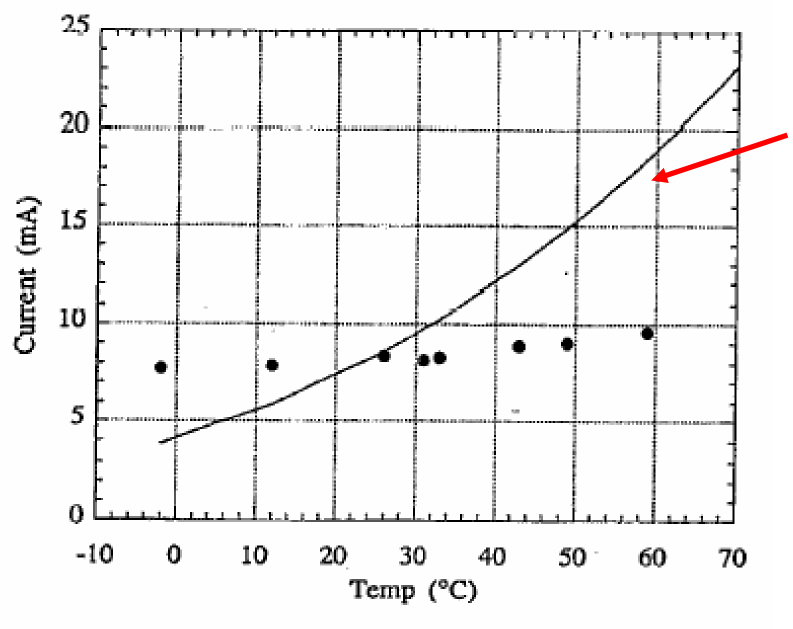


The current is controlled by the hole injection

I. D. Parker JAP 75, 1656 (1994)

Temperature dependence of the I-V characteristics

ITO/MEH-PPV/Au @ 17V



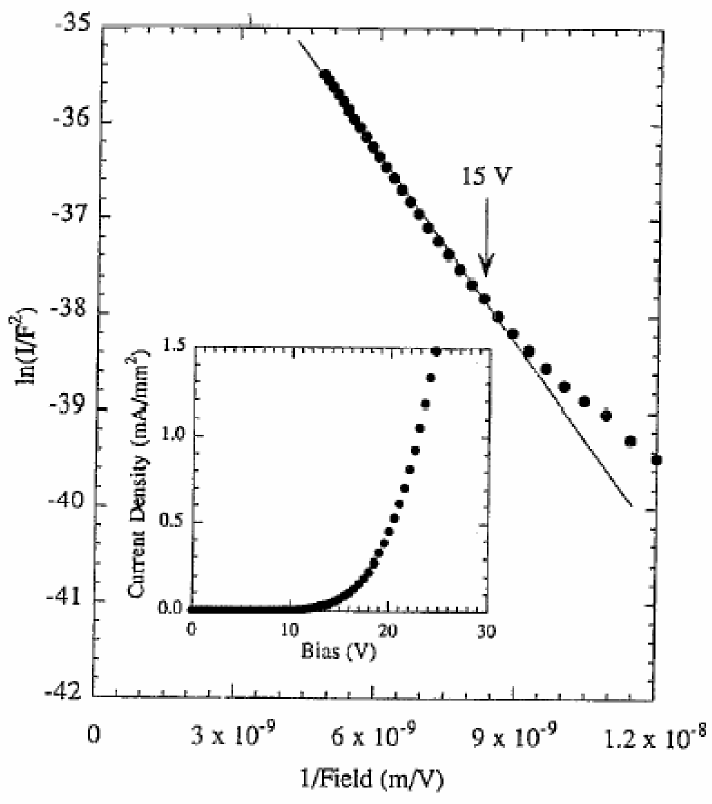
0.2 eV Schottky barrier device

The injection current is not likely due to thermionic emission

I. D. Parker JAP 75, 1656 (1994)

Fowler-Nordheim Plot

ITO/MEH-PPV/Au



$$I \propto F^2 \exp\left(\frac{-\kappa}{F}\right)$$

$$\kappa = \frac{8\pi\sqrt{2m^*}\varphi^{3/2}}{3qh}$$ for a triangular barrier

φ : the barrier height

m* : the effective mass

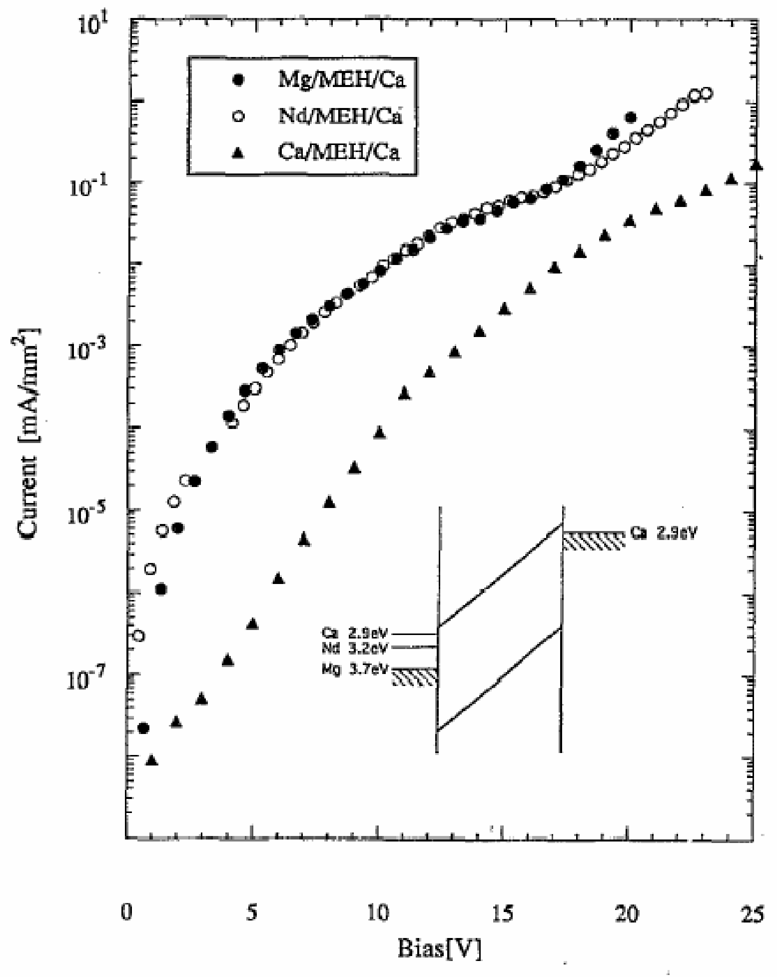
TABLE II. The barrier height inferred from the Fowler–Nordheim analysis for a range of "hole-only" devices.

Device structure	Barrier height (eV)
ITO/MEH-PPV/In	0.21–0.23
ITO/MEH-PPV/Ag	0.28–0.33
ITO/MEH-PPV/Al	0.22–0.24
ITO/MEH-PPV/Cu	0.22–0.26
ITO/MEH-PPV/Au	0.19–0.22

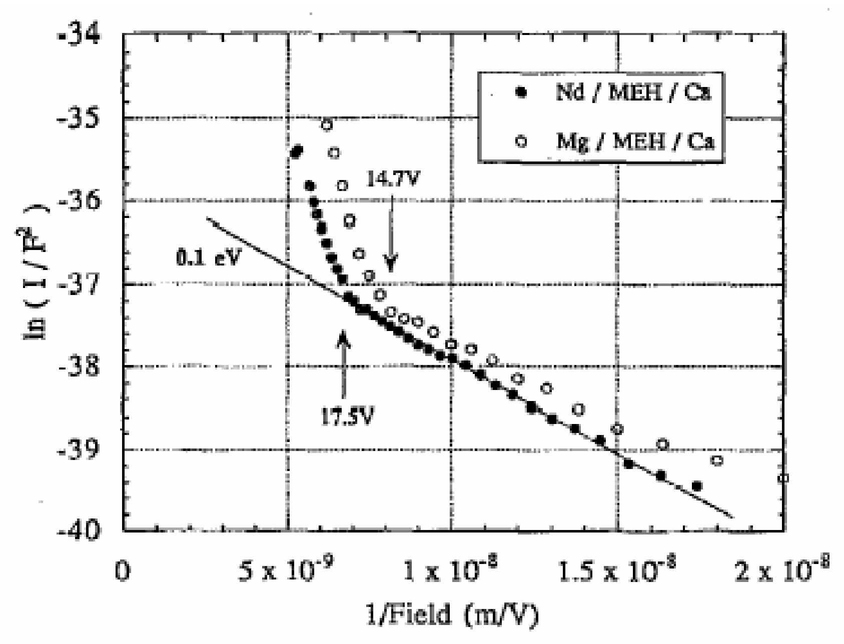
constant barrier height ~ 0.2-0.3 eV

I. D. Parker JAP 75, 1656 (1994)

“Electron-only” device



Fowler-Nordheim Plot



I. D. Parker JAP 75, 1656 (1994)

Device efficiency vs cathode work function

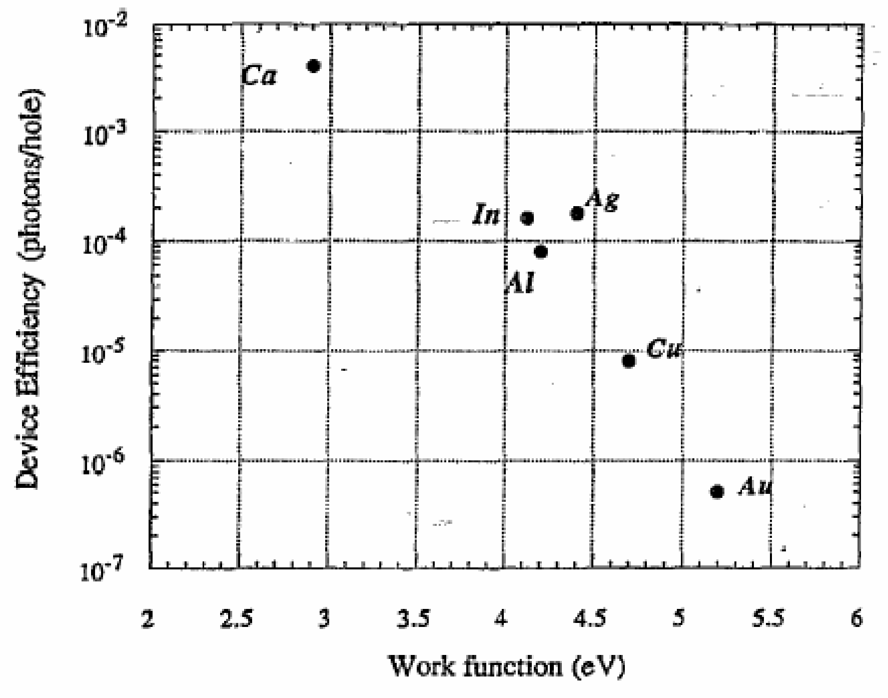
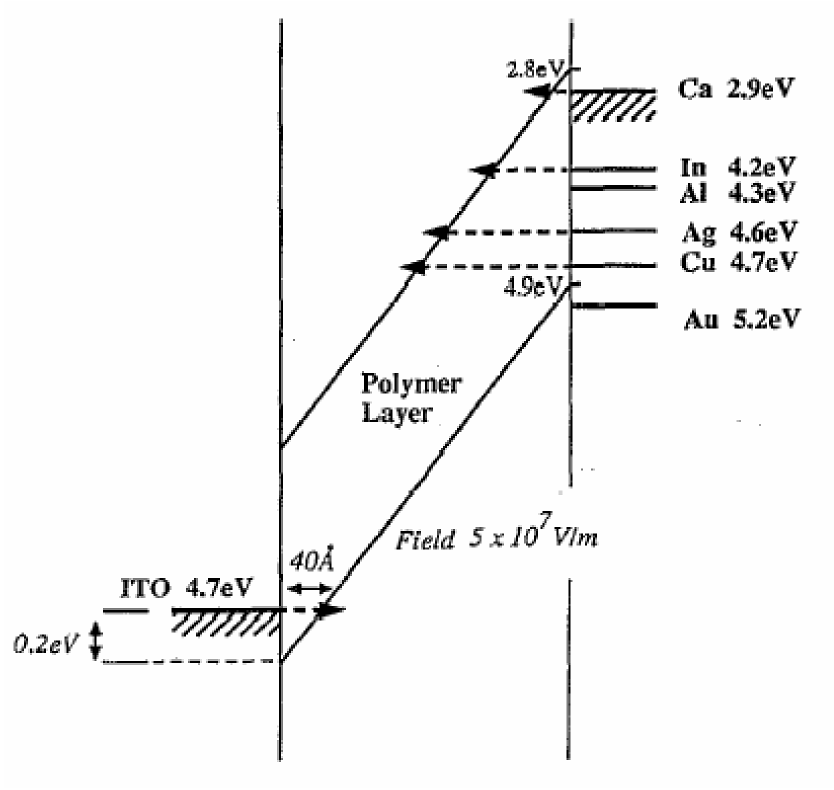


TABLE I. External quantum efficiency for ITO/MEH-PPV LEDs with various cathode materials.

Metal	Work function (eV)[a]	Band offset (eV)	Efficiency (photons/hole)
Ca	2.87–3.00	~0.1	4×10^{-3}
In	4.12–4.20	1.3–1.4	1.6×10^{-4}
Ag	4.26–4.74	1.5–1.9	1.8×10^{-4}
Al	4.06–4.41	1.2–1.6	8×10^{-5}
Cu	4.65–4.70	1.9	8×10^{-6}
Au	5.1–5.47	2.3–2.7	5×10^{-7}

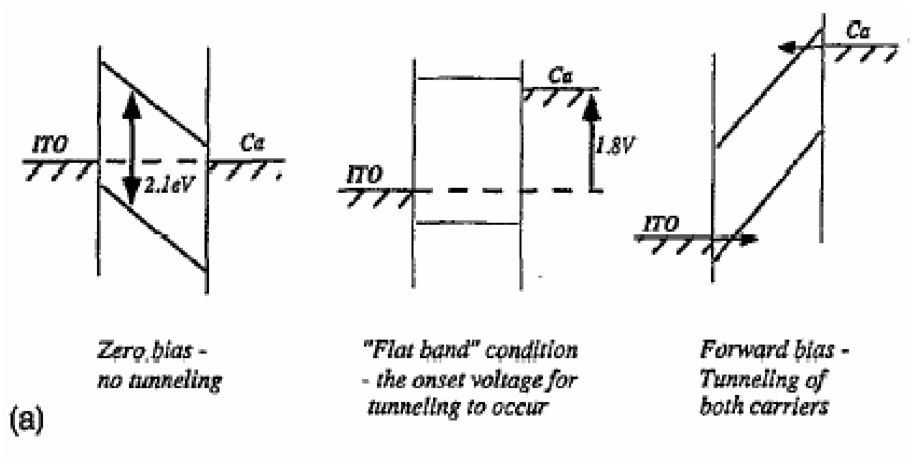
I. D. Parker JAP 75, 1656 (1994)

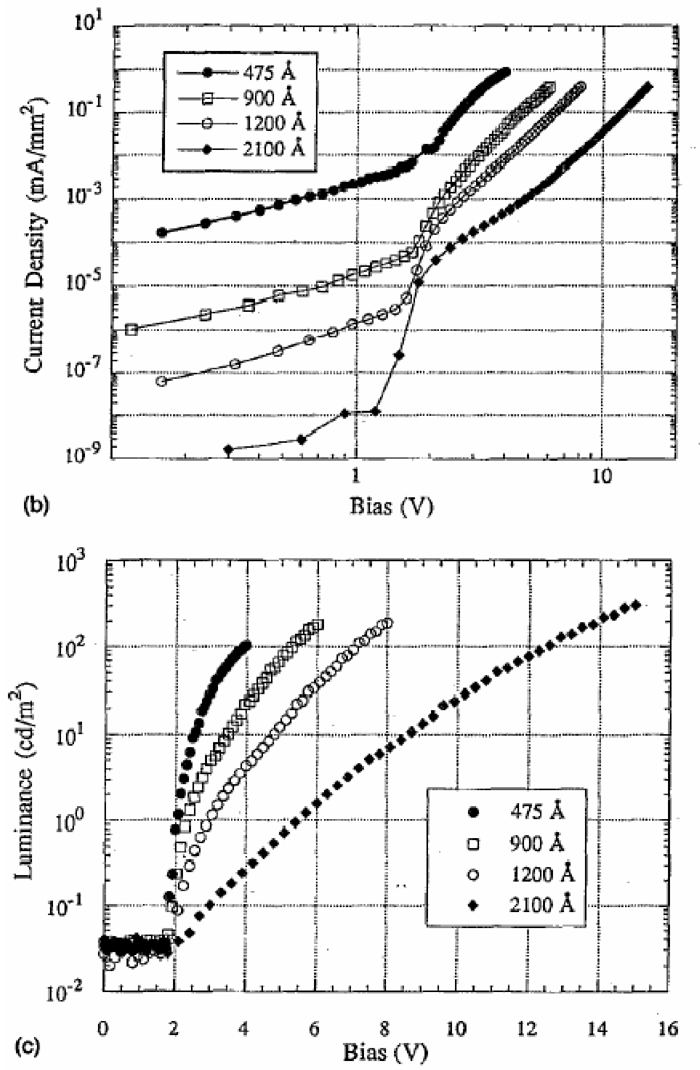
The band diagram of the model



in forward bias

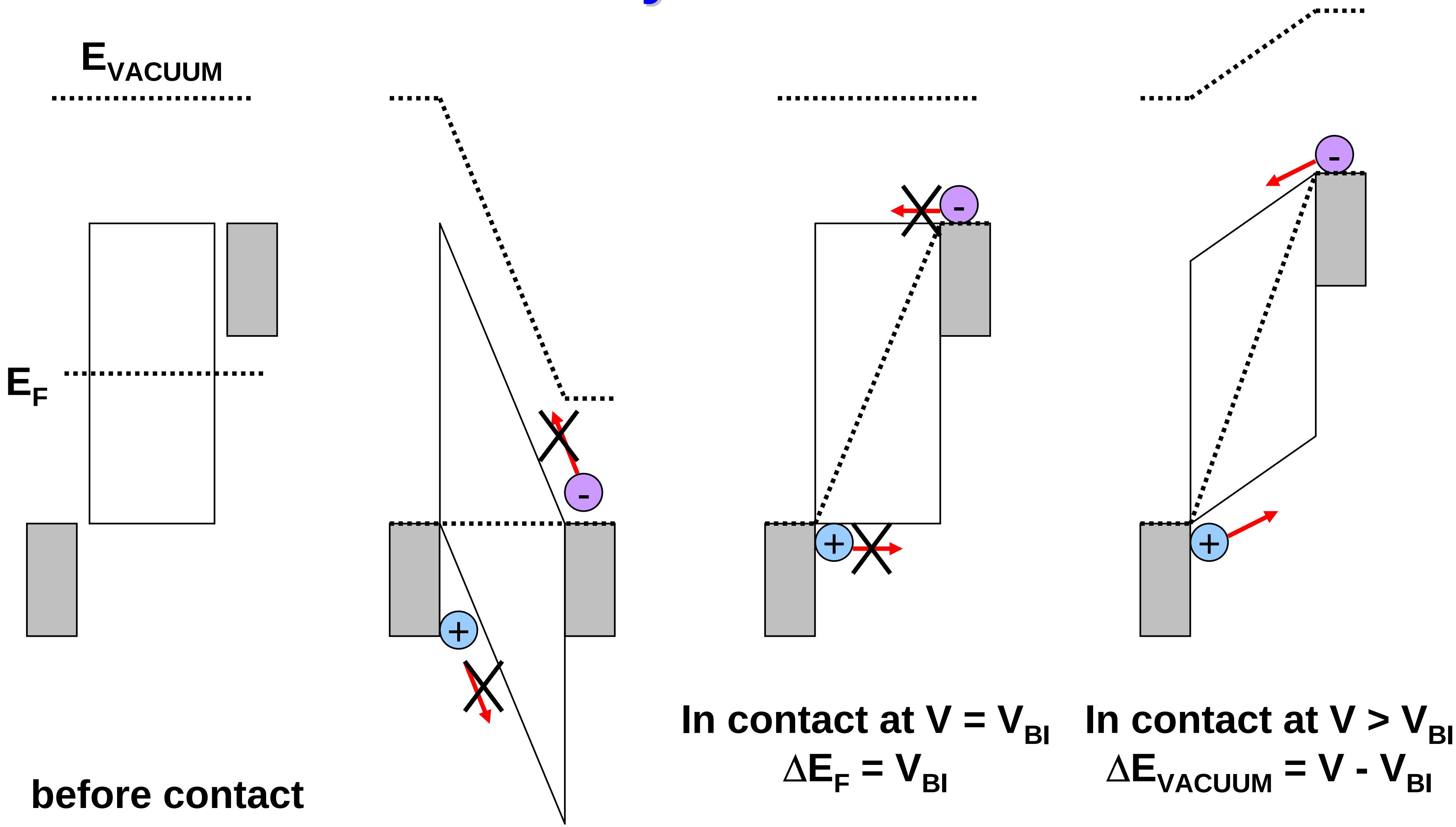
The band diagram of the model





The rigid band model seems appropriate, since little band bending occurs.
The device immediate depletion due to low carrier concentration (<10^{14} cm^3)

Summary of J-V curve



before contact

In contact at equilibrium
$\Delta E_F = 0$; $V = 0$

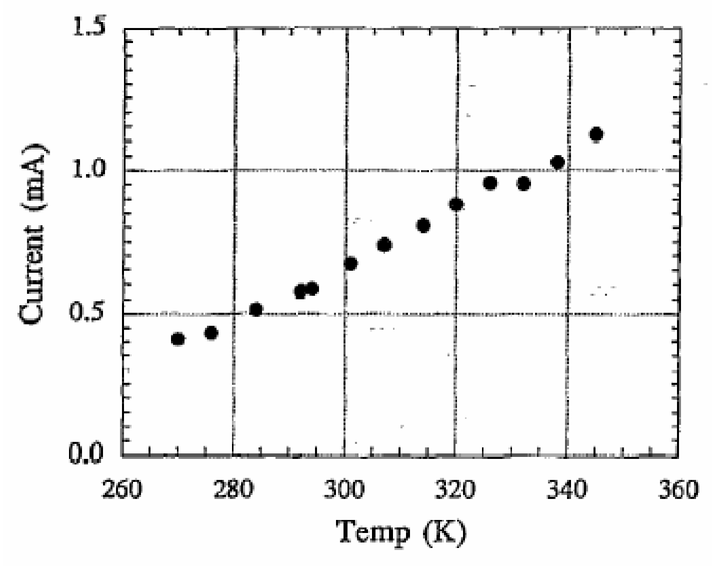
In contact at $V = V_{BI}$
$\Delta E_F = V_{BI}$

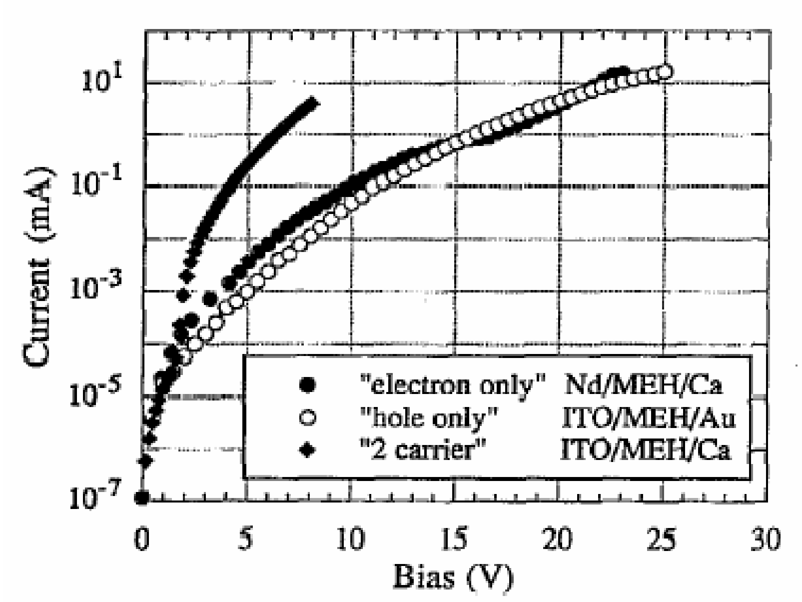
In contact at $V > V_{BI}$
$\Delta E_{VACUUM} = V - V_{BI}$

$V_{BI} \sim \phi_{anode} - \phi_{cathode}$

Limits the model

ITO/MEH-PPV/Ca





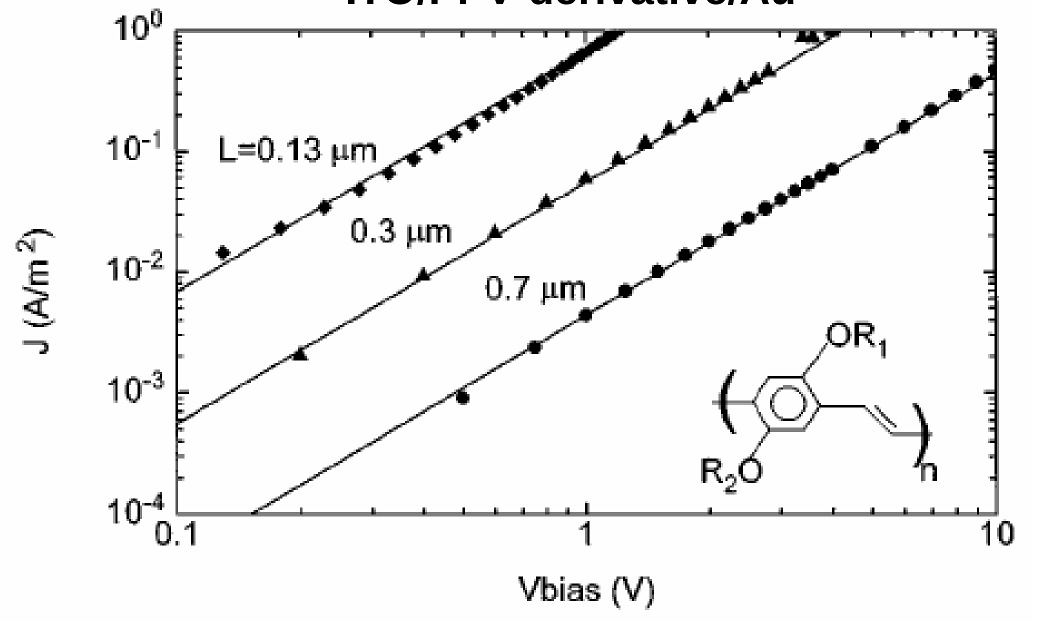
weak temp. dependence injection current due to the low injection barrier height

space-charge limiting effect

The barrier height for electron injection ~ 0.1eV (4kT)

An alternative model

ITO/PPV-derivative/Au



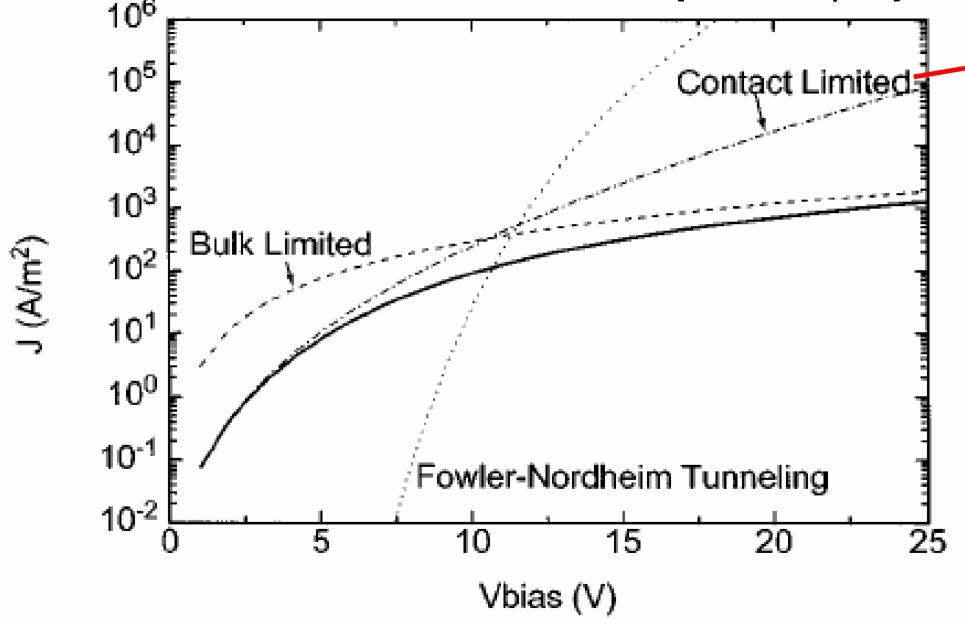
The I-V characteristics follows SCLC : $J = \frac{9}{8} \epsilon_0 \epsilon_r \mu_p \frac{V^2}{L^3}$

μ = 5 x 10^{-7} cm^2/V.s

P. W. Blom, *et al*. Appl. Phys. Lett. 68, 3308 (1996)

An alternative model

ITO/PPV-derivative/Au (L = 0.1 μm)



Themionic emission-diffusion theory :

$$J = qN_c\mu F(0)\exp\left(-\frac{q\phi_b}{kT}\right)$$

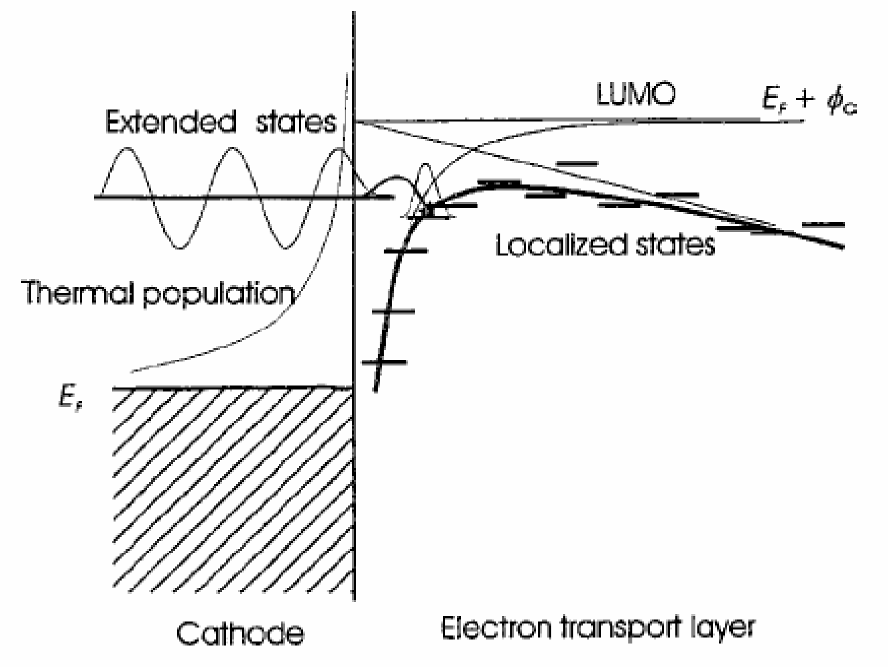
$F(0)$ the electric field at the contact

At low bias, diffusion-limited injection;
At high bias, space-charge effects dominate.

In general, it depends on both ϕ_{b0} and L whether the conduction is injection or space-limited
SCLC is usually observed if ϕ_{b0} < 0.2 V

P. W. Blom, *et al*. Appl. Phys. Lett. 68, 3308 (1996)

Energetics of the charge injection process



The barrier height
The image potential
The potential due to the interfacial electric field
A random component due to disorder
(the mean free path is of order of molecular distance)

J. C. Scott, J. Vac. Sci. Technol. A 21, 521, (2003)

Two extreme types of carrier motion in solids

Highly delocalized plane wave in a broad carrier band

e.g. Ge, bandwidth (W) ~ 3 eV,

scattering time $\tau \sim m\mu/e \sim 10^{-3}$ sec

mean free path ~ 100 nm >> atomic separation (0.25nm)

$\mu \gg 1\ cm^2V^{-1}sec^{-1}$

$\mu \propto T^{-n}$ (n>1)

Localized charges moving by hopping

bandwidth (W) $\leq$ kT

being scattering virtually at every step

$\mu \ll 1\ cm^2V^{-1}sec^{-1}$

$\mu \propto \exp(-E/kT)$ (E : activation energy)

Molecular crystals : falls in an intermediate category

$\mu \sim 1\ cm^2V^{-1}sec^{-1}$

Transport mechanisms in solids

Main difference:

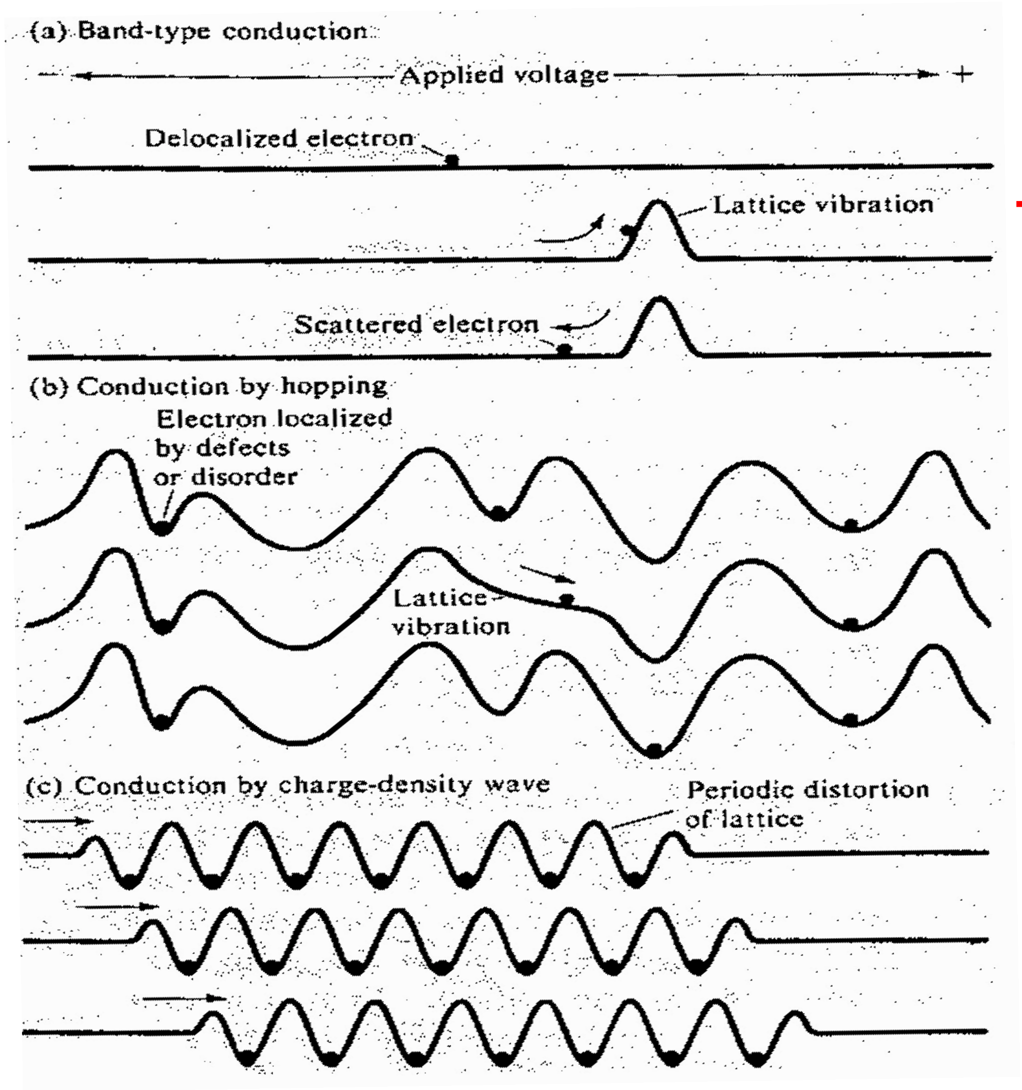
Phonon scattering limited

$\mu = a\,T^{-n}$

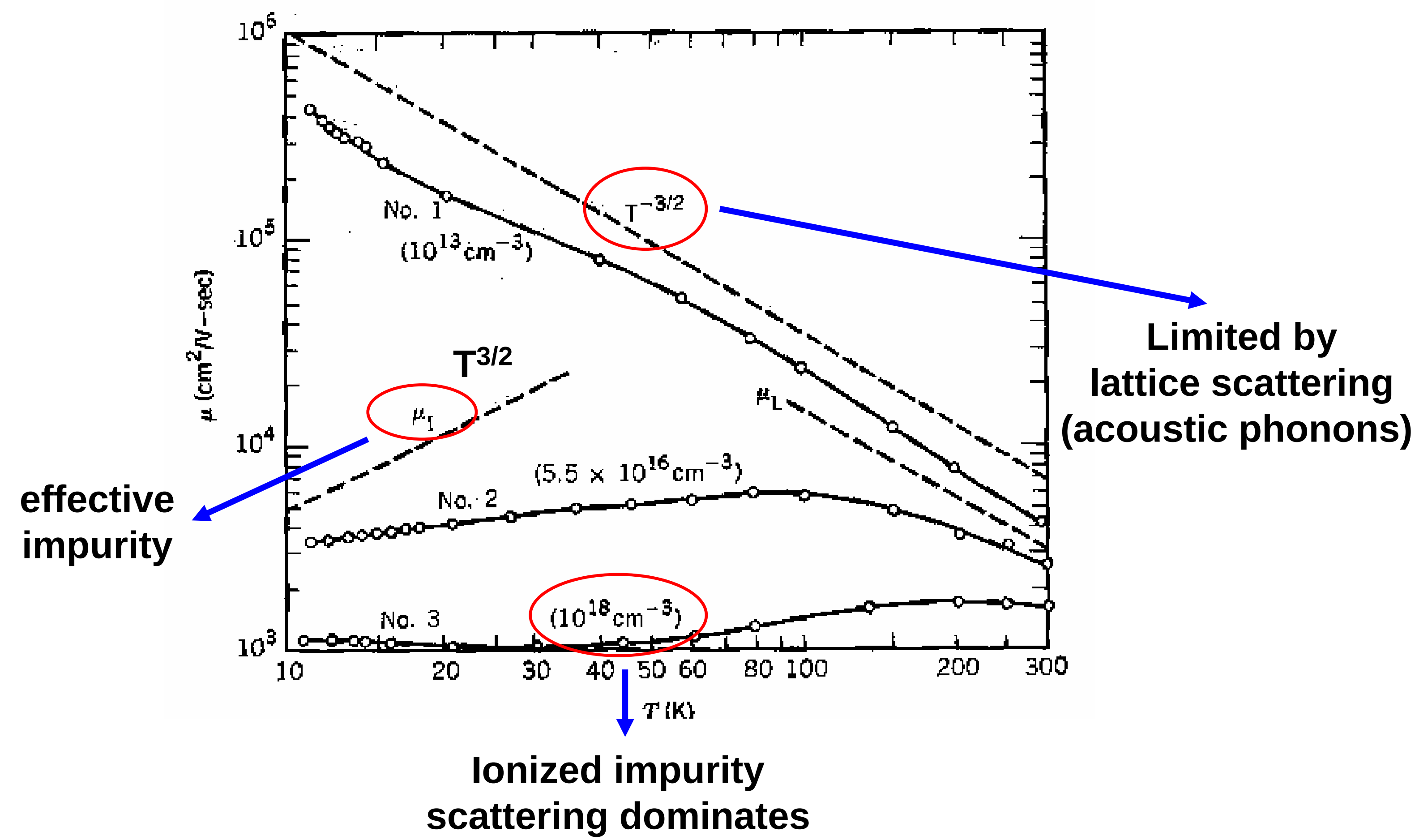
$(n \sim 1)$

Phonon assisted

$\mu = \mu_o \exp -(E_a/kT)$



Electron mobility in n-type Ge at different temp. For various doping levels

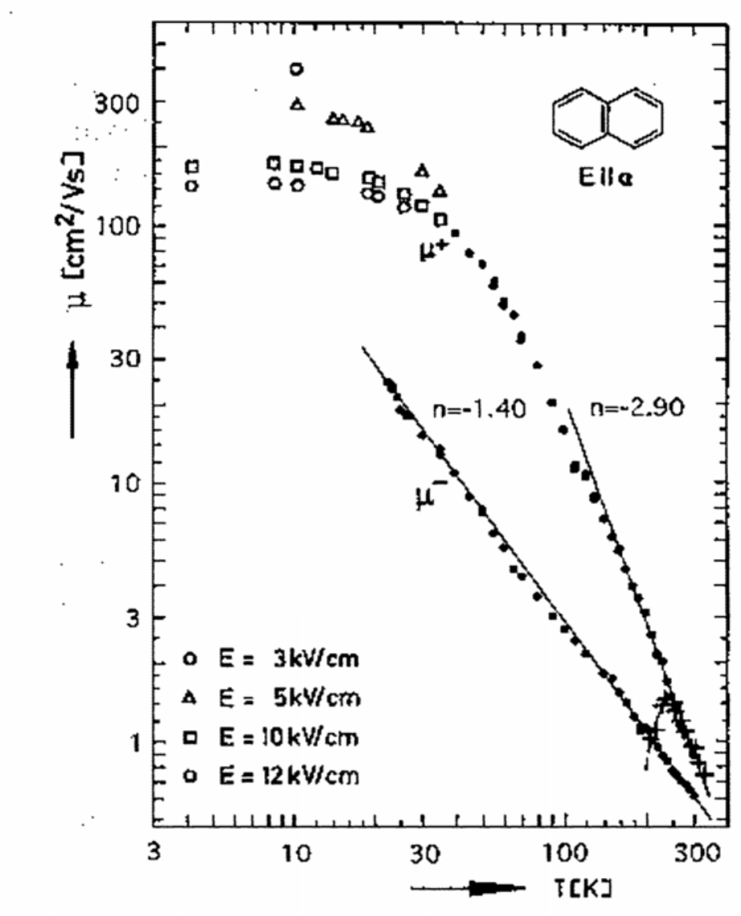


M. S. Tyagi, Introduction to semiconductor materials and devices, Chapter 4

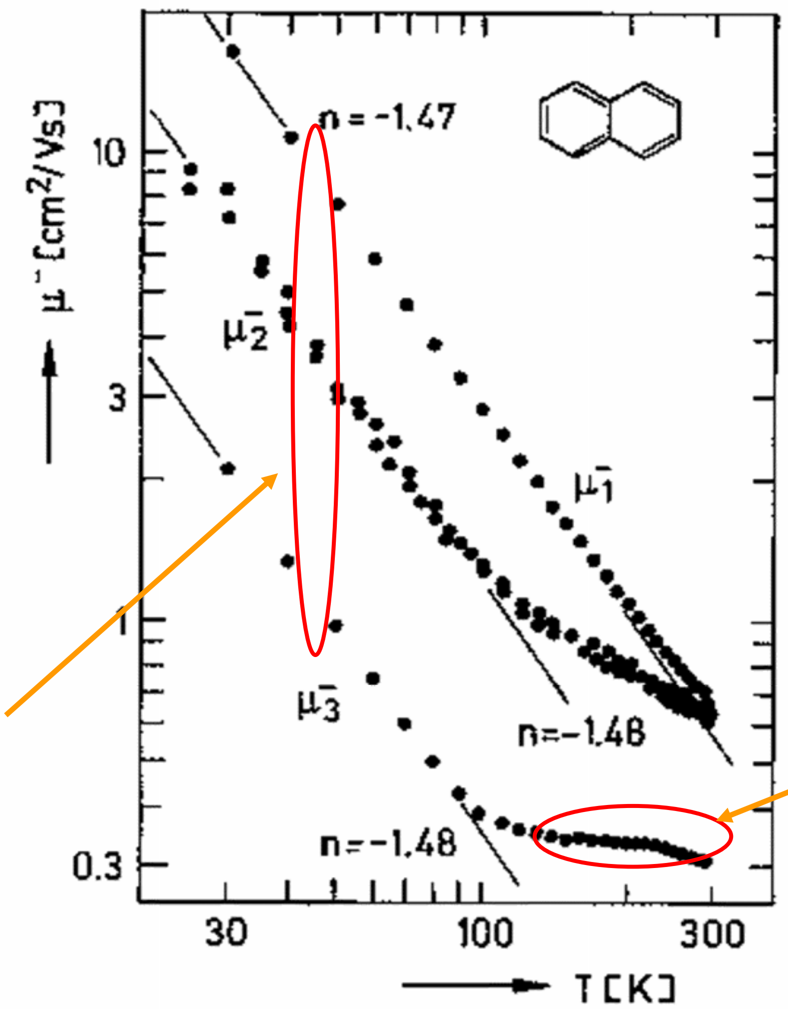
Ultrahigh pure single crystal of polyenes

At low temperature, coherent bandlike transport become the prevalent Transport mechanism.

e.g. ~400 $cm^2V^{-1}sec^{-1}$ (hole) in single crystal naphthalene at 4K



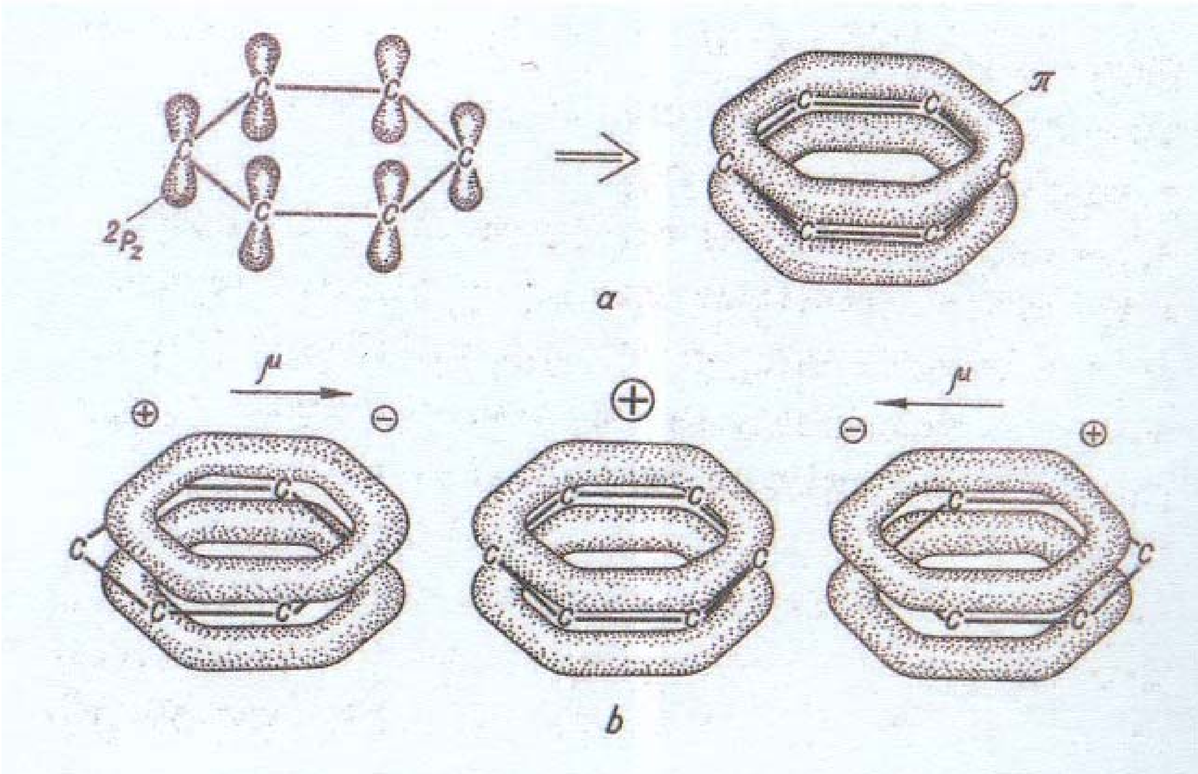
Anisotropic electron nobilities of organic crystals



band-like transport

polaron-like transport

Strong electronic polarization



formation of induced dipoles μ on neutral molecules of the crystal in the field of a localized positive charge carrier

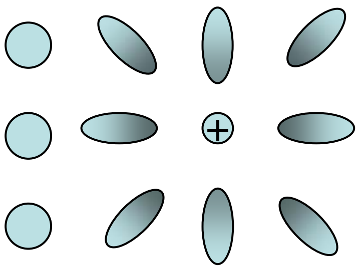
T. N. Jackson, SID seminar notes, 2004

Polarons

Strong-phonon-electron coupling → a localized polaron

π orbitals of organics has high polarizability

The typical charge-carrier localization time is several order of magnitude greater than the relaxation time for electronic polarization of the surrounding lattice molecules



The charge move together with their electronic polarization "cloud"

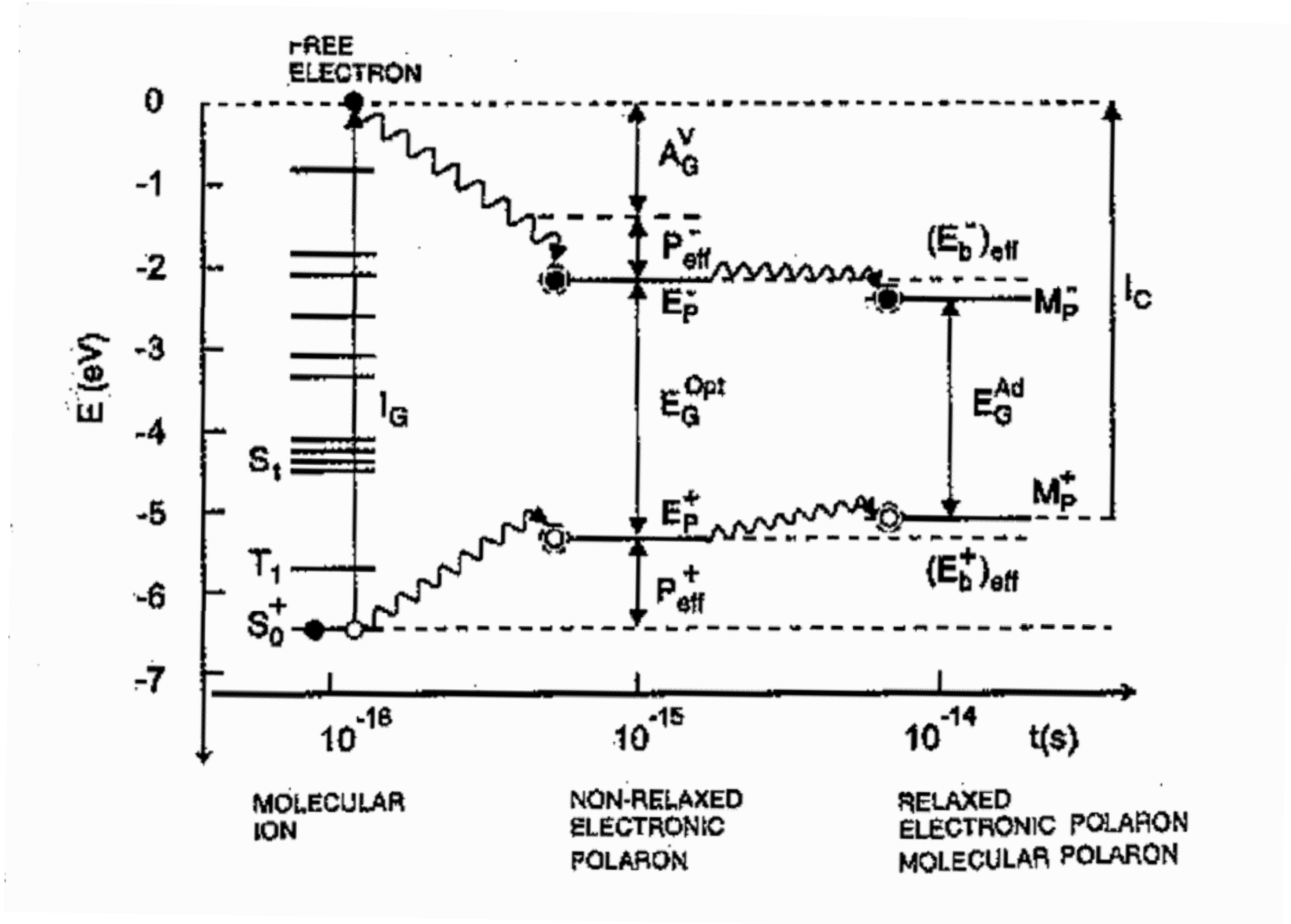
The quasifree charge carriers are called Polarons

The charge carrier motion should be described in the framework of a hopping model (self-trapped in the polarization well)

Ways to create Polarons:

Charge injection, chemical doping, thermal excitation, and optical excitation

Electronic Polarons vs Molecular Polarons



E_p^- & E_p^+ : **non-relaxed electronic polaron** states

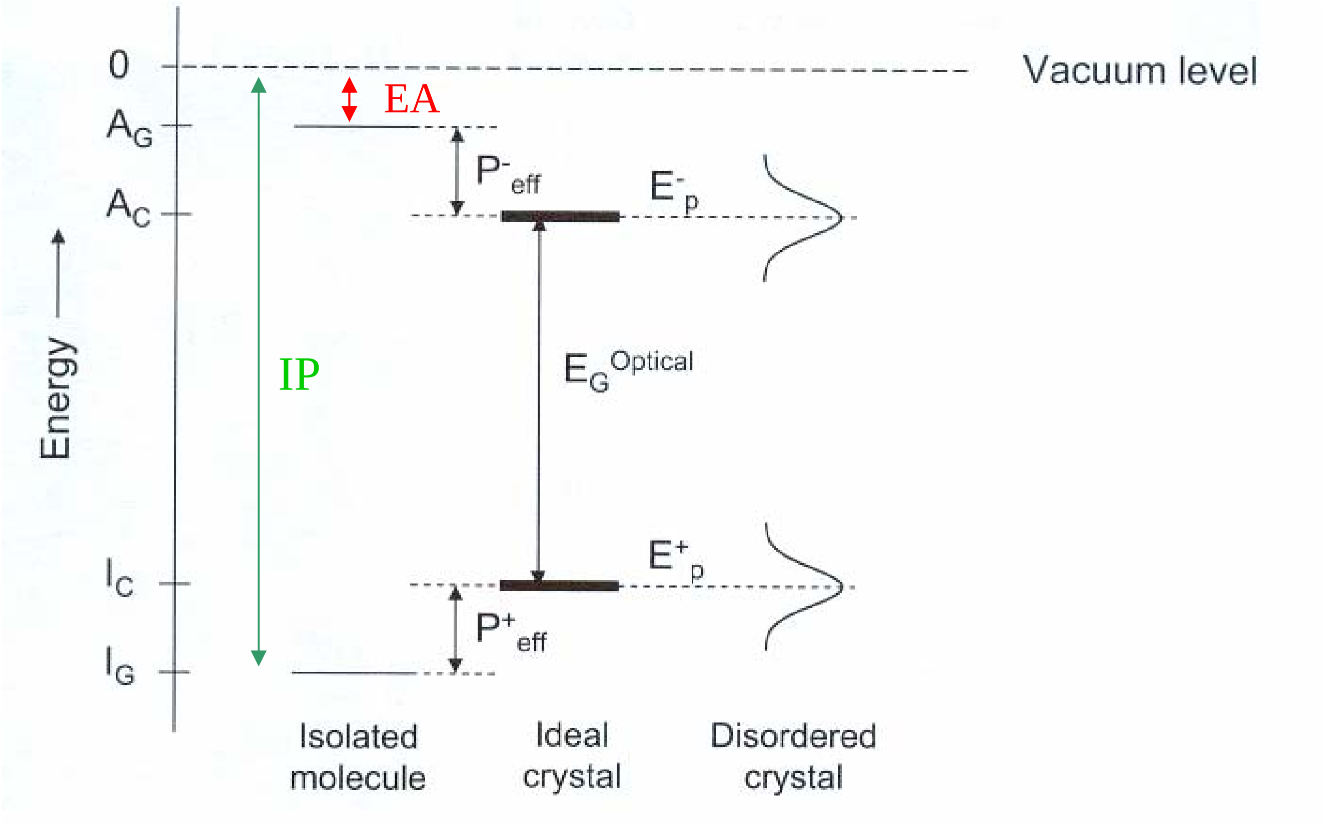
P_{eff}^- & P_{eff}^+ : effective electronic polarization energies

M_p^- & M_p^+ : **molecular polaron** conductivity levels

$(E^-)_{eff}$ & $(E^+)_{eff}$: effective formation energies of a molecular polaron (due to vibronic polarization)

R. Farchioni & G. Grosso, Organic Electronic Materials (Wiley, New York, 1981)

Energy Bands in Organic Molecular Crystals



I_c : molecular crystal ionization potential

A_c: molecular crystal electron affinity

E_p^- & E_p^+ : electronic polaron energy level

P_{eff}^- & P_{eff}^+ : effective electronic polarization energies

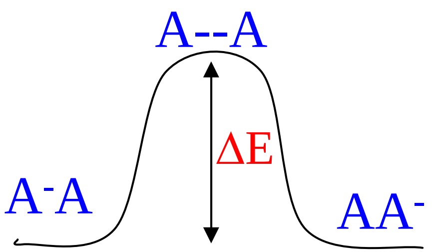
T. N. Jackson, SID seminar notes, 2004

Hopping mechanism of charge transport

For polaron-type transport,

$\sigma = \sigma_o \exp(-\Delta E/2kT)$

ΔE : the activation energy



(no energy exchange)

Phono-activated hopping mechanism

$A^{-}A \longleftrightarrow$ "$A^{-}A$" $\overset{k_{ET}}{\longleftrightarrow}$ "AA^{-}" $\longleftrightarrow AA^{-}$

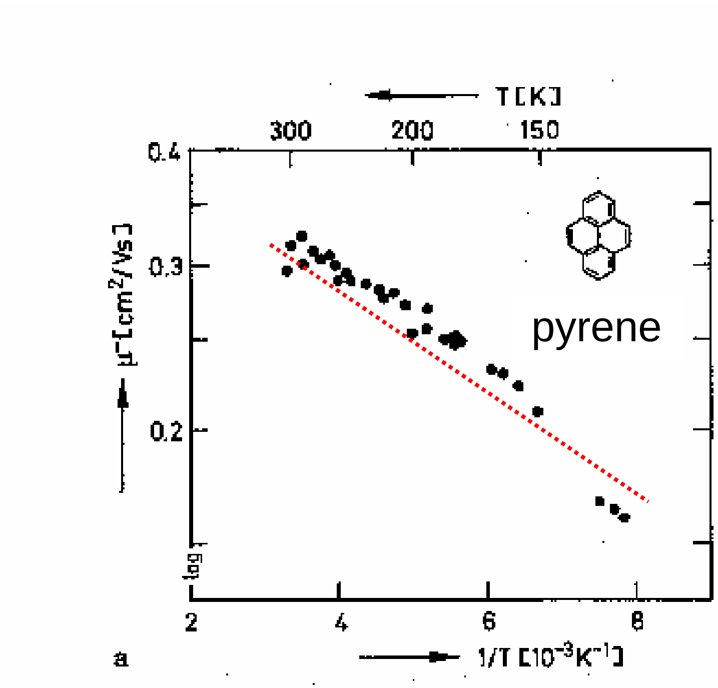
k_{ET} : rate-constant of electron transfer
depends on the electronic overlaps of the pair of molecules

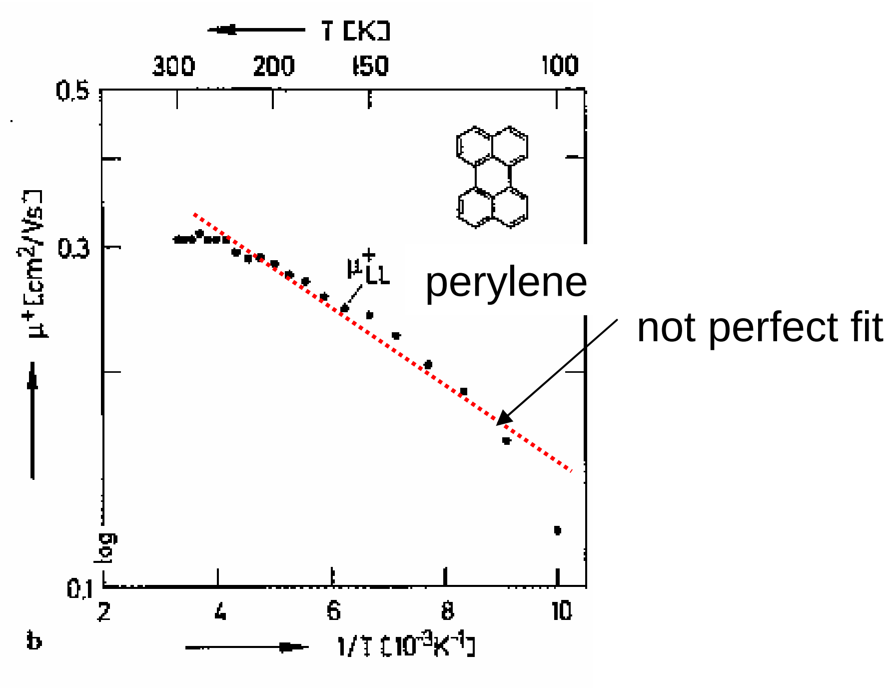
$\mu = \mu_o \exp(-\Delta E/kT)$

ΔE : the activation energy

$\longrightarrow$ $$\log(\mu) = \frac{-\Delta E}{k} \frac{1}{T}$$

Arrhenius plot of the mobilities of organic materials





$$\log(\mu) = \frac{-\Delta E}{k}\,\frac{1}{T}$$

Some highly purified organic materials are based on polaron hopping

Two general types of organic materials

Two general cases

- **“Low” mobility materials**
  - transport via hopping
  - typical mobility $10^{-6} \sim 10^{-1}$ $cm^2V^{-1}sec^{-1}$
  - common for polymeric or disorder organic semiconductors

- **“high” mobility materials**
  - transport via narrow band transport
  - typical mobility $10^{-1} \sim 10$ $cm^2V^{-1}sec^{-1}$
  - $\mu(T)$ depends on details (traps, doping, bandwidth, etc.)
  - common for small molecular crystal organic semiconductors