Sobre la TERMOELECTRICIDAD
y la
FÍSICA en la NANOESCALA
o
Sobre como encender una bombilla con un mechero

Javier Rodríguez Viejo
Departament de Física
Universitat Autònoma de Barcelona

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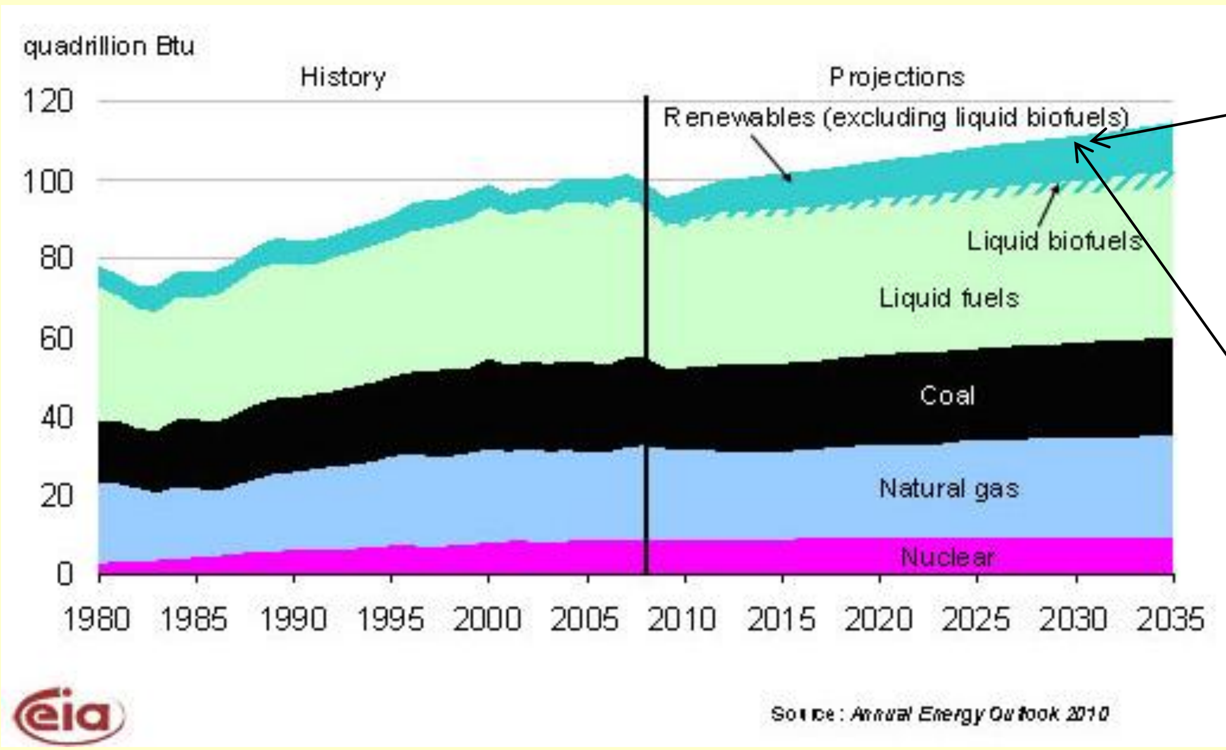
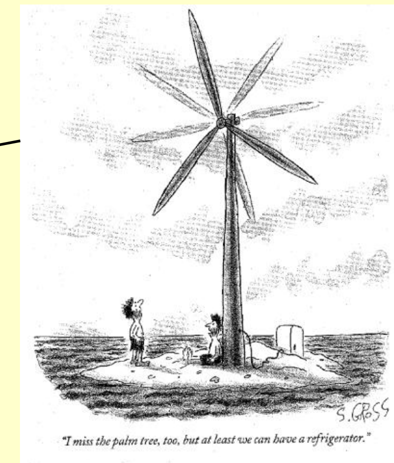
El problema de la ENERGÍA

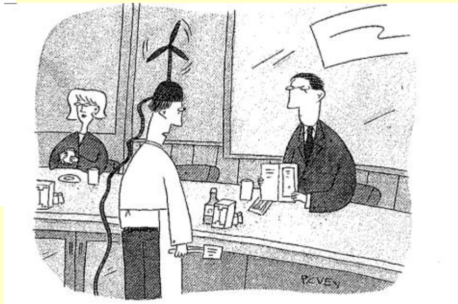
En 2008 la potencia energética promedio consumida a nivel mundial fue 15 TW = $1{,}5\times10^{13}$ W ; en energía 474 exajulios 474×10^{18} julios





m= 70 Kg
v= 20 km/h

100-200 W
durante 1h



"I cook everything with an alternative energy source, so it may take a while."

Población 7000 millones

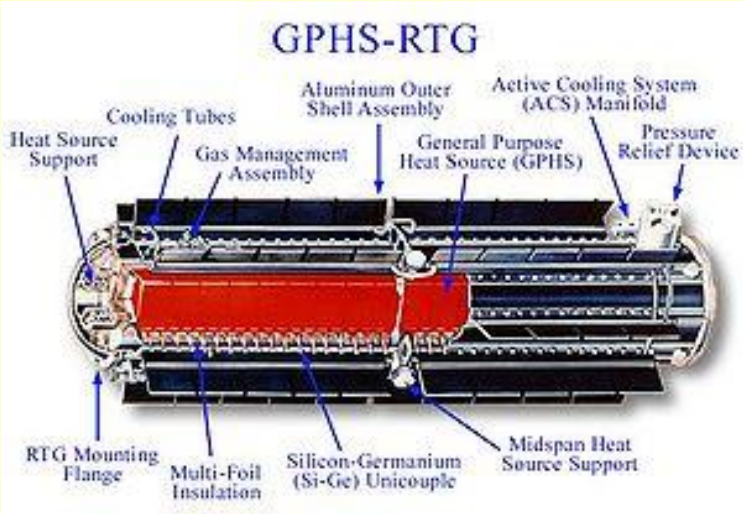
15 TW

2 kWh por persona!!!

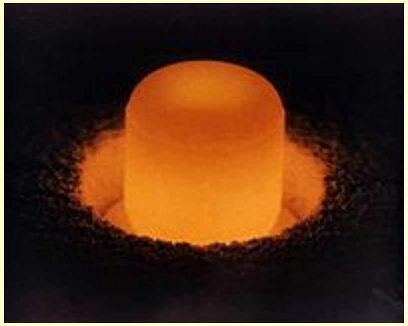
¿Qué papel puede jugar la termoelectricidad?

¿Podemos usarla como una fuente viable de producción energética?

Aplicaciones actuales de la termoelectricidad -- I



Generador Termoeléctrico de Radioisótopos



Desintegración radioactiva del ^{238}Pu en partículas alfa.

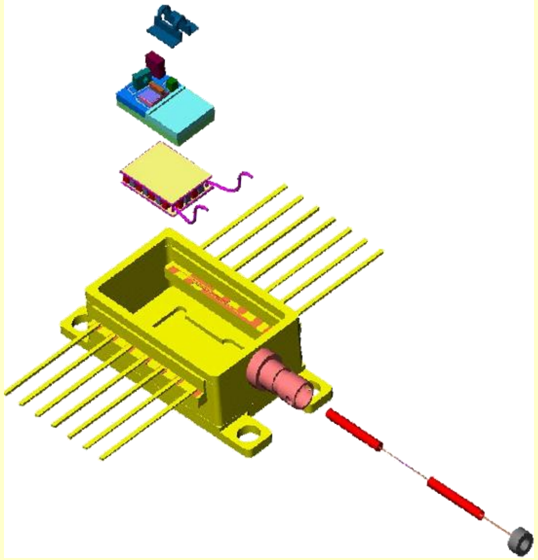
Aplicaciones actuales de la termoelectricidad -- II

12V refrigerador/calefactor de tazas/latas

Reloj termoeléctrico

Sistema de control de Temperatura en vehículos

Refrigeración de láseres



Sistemas de visión nocturna por infrarrojos

El 60% de la energía primaria consumida a nivel mundial se disipa en forma de calor de deshecho

Useful Heat

Free Electricity

Heat Generator

Power Recovery Device

Waste Heat

Guión

- **Curso básico (y acelerado) de Materiales**

- **Termoelectricidad: Algo de historia.**

- **Materiales termoeléctricos: ¿Qué son y para qué sirven?**

- **Eficiencia, eficiencia, eficiencia:**
  En busca del Santo Grial. Figura de mérito = 3.

- **y aparece la Nanotecnología y, la Física en la Nanoescala.**

- **Materiales de baja dimensionalidad**

- **Perspectivas**

Curso básico (y acelerado) de Materiales

Metales

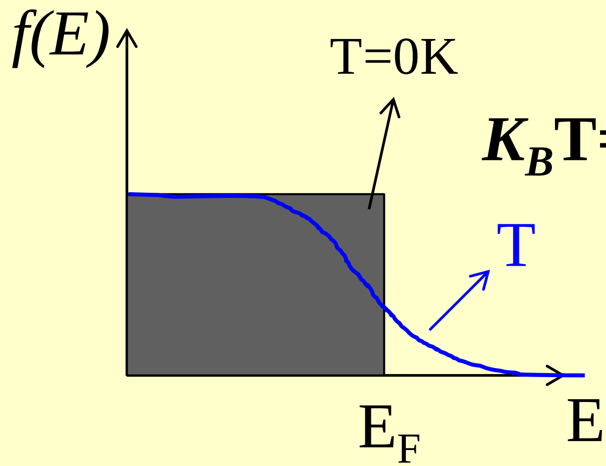
Presencia de electrones libres

⇓

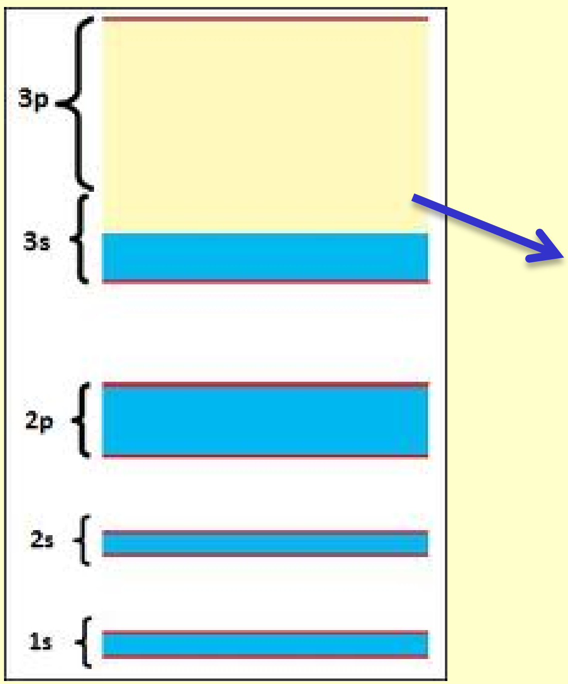
Buenos conductores electricidad

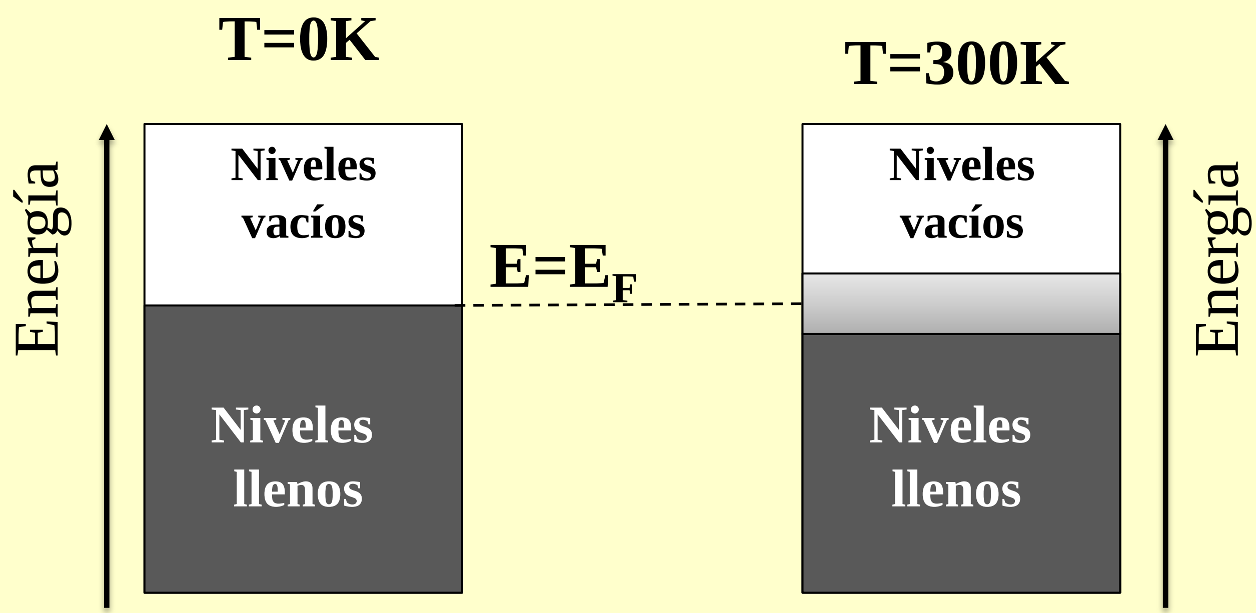
Buenos conductores del calor

Estadística de Fermi



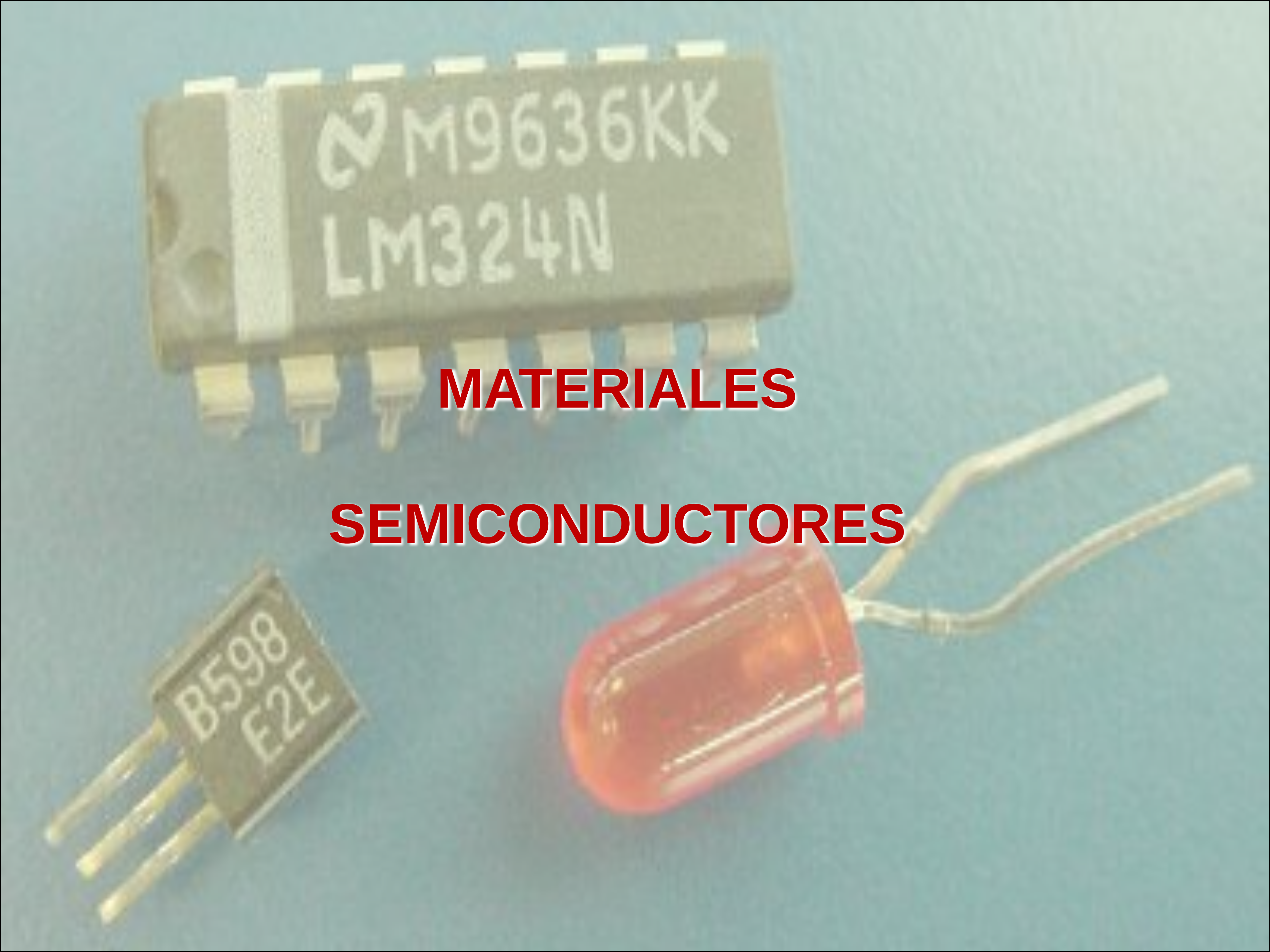
$K_B T = 30\ \text{meV}$

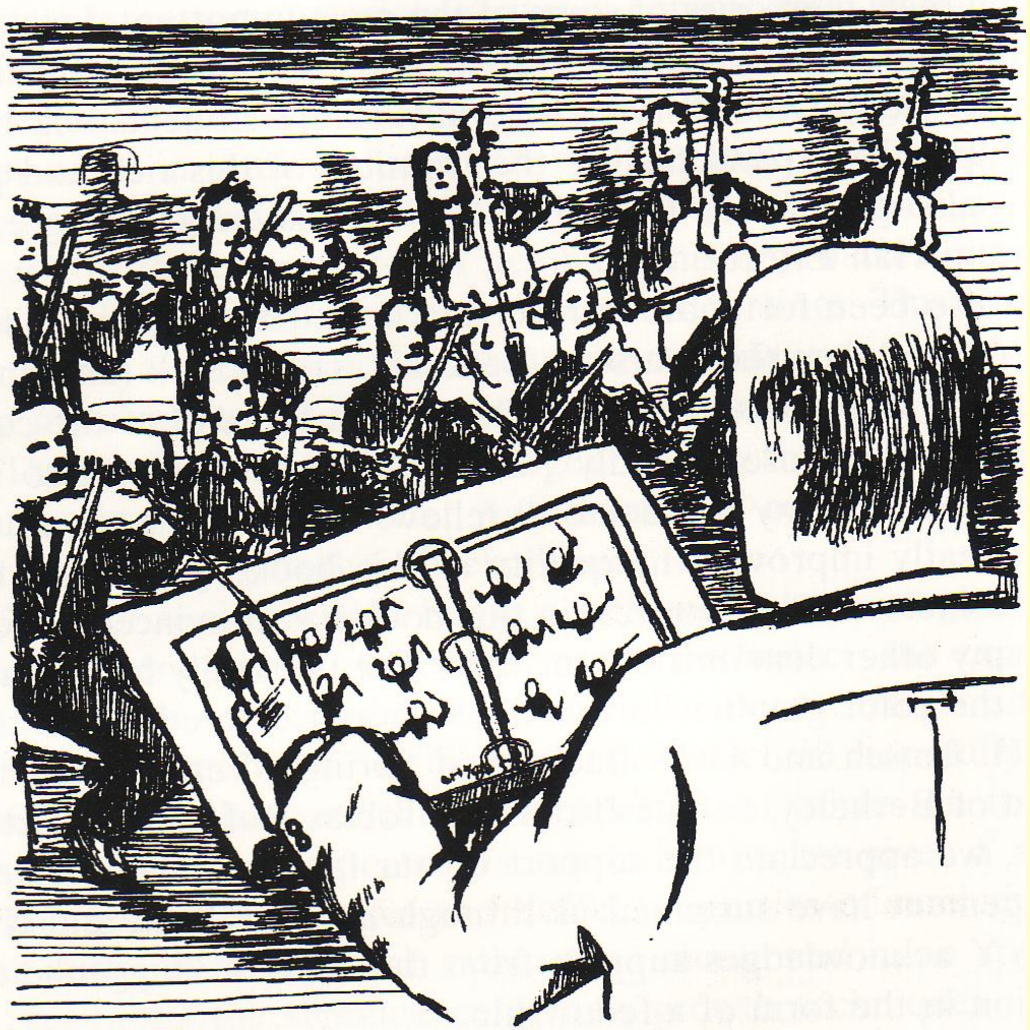




MATERIALES

SEMICONDUCTORES

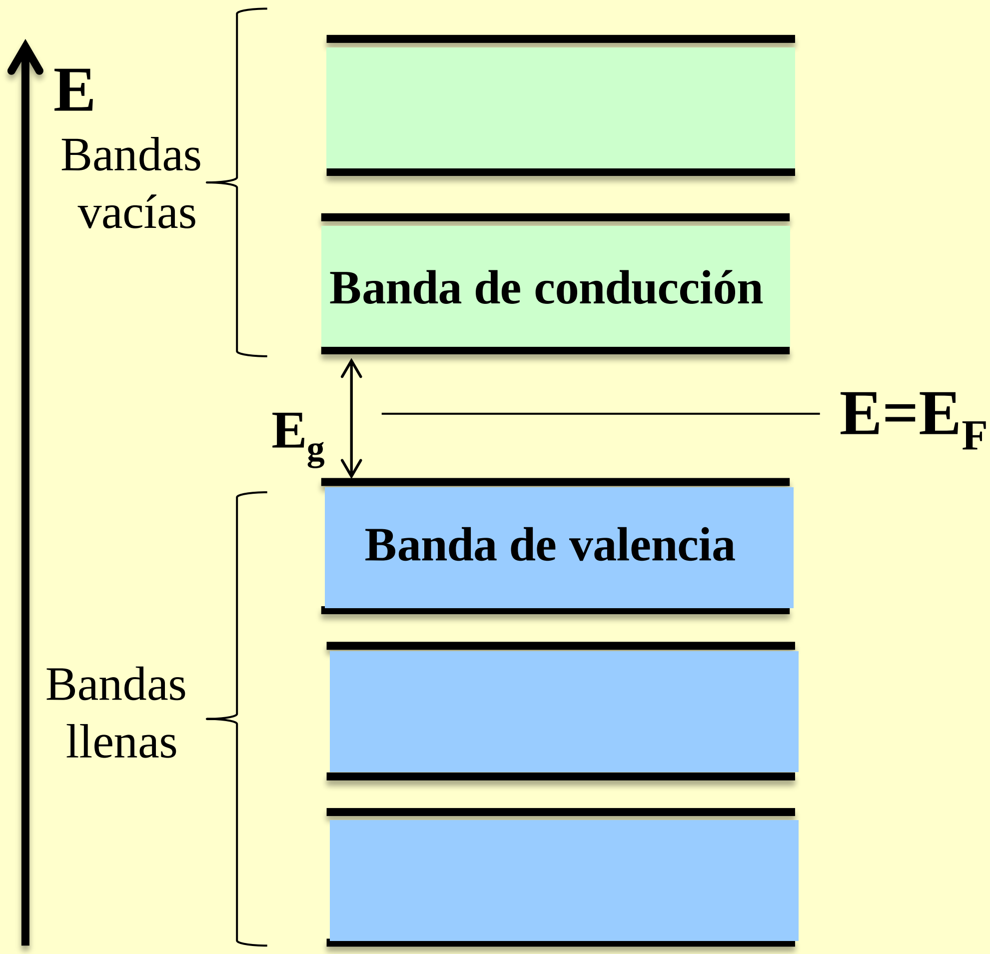




A SEMI-CONDUCTOR

M.Cardona, P.Yu
Optical properties of semiconductors

SEMICONDUCTORES



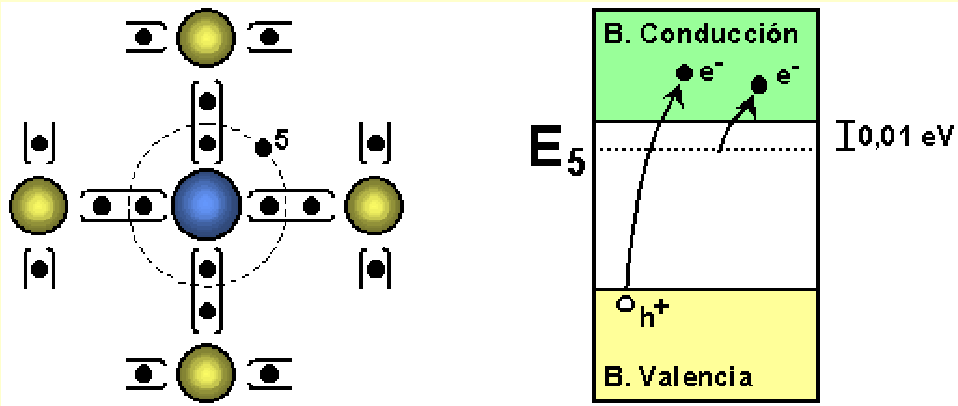
Valores de brecha de energía para algunos semiconductores

Cristal	E_g (eV) 0 K	E_g (eV) 300 K
Si	1.17	1.14
Ge	0.744	0.67
InP	1.42	1.35
GaP	2.32	2.26
GaAs	1.52	1.43
CdS	2.58	2.42
ZnO	3.43	3.20

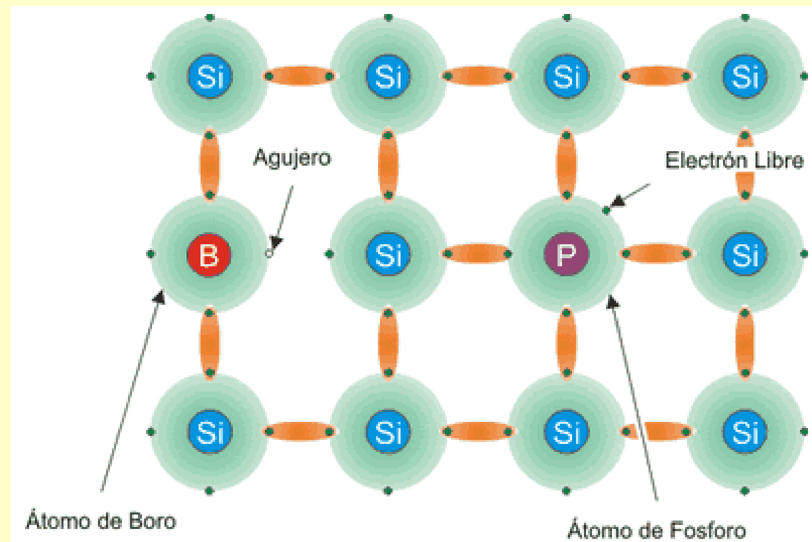
$0{,}1 < E_g < 4$ eV $K_B T = 30$ meV

DOPAJE DE SEMICONDUCTORES

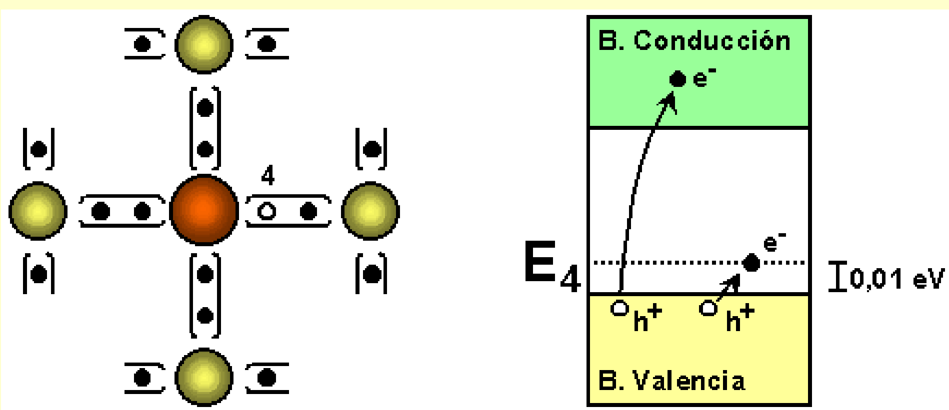
Dopaje tipo n



conducción por electrones

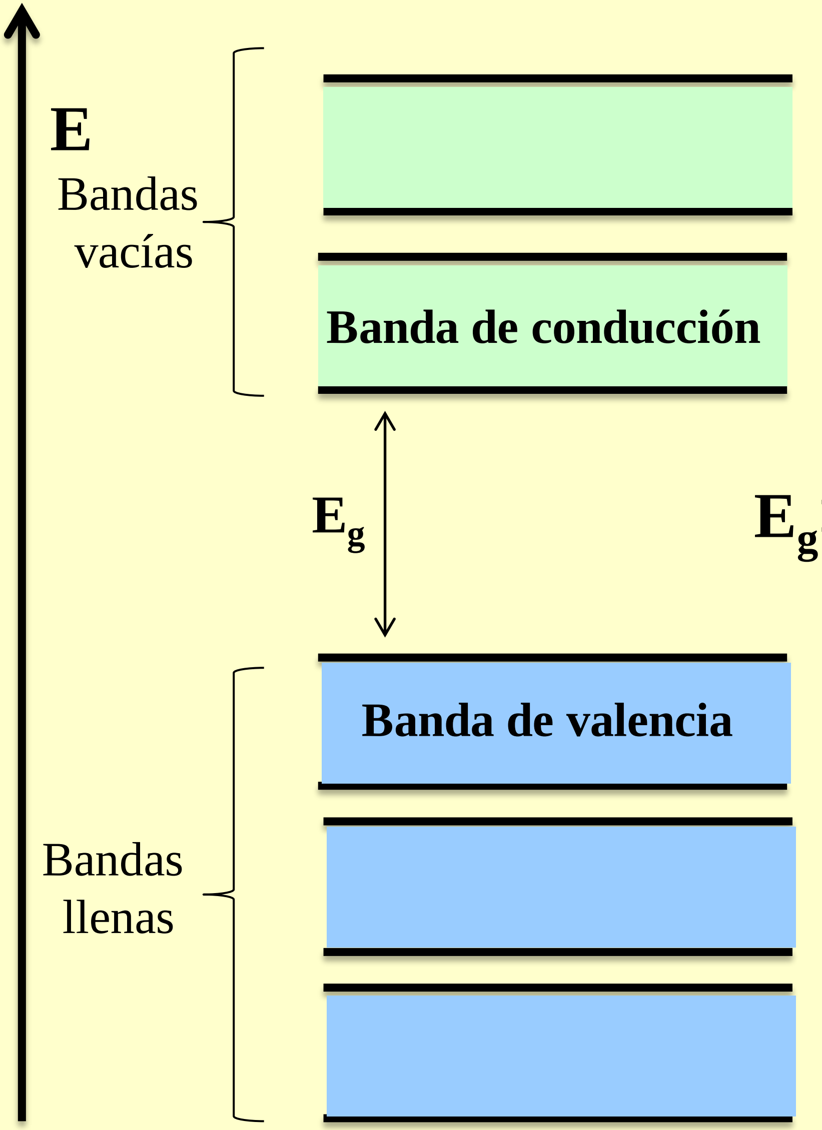


Dopaje tipo p



conducción por huecos

AISLANTES



E_g>4 eV

E_g=9 eV

Termoelectricidad

Térmica → Eléctrica

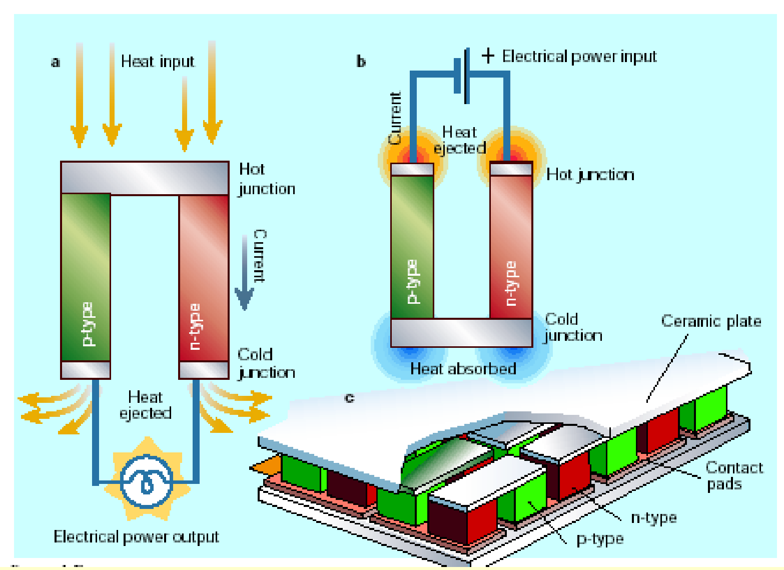
Calor → corriente eléctrica

Eléctrica → Tèrmica

Corriente → refrigeración

Thomas Seebeck
1770-1831

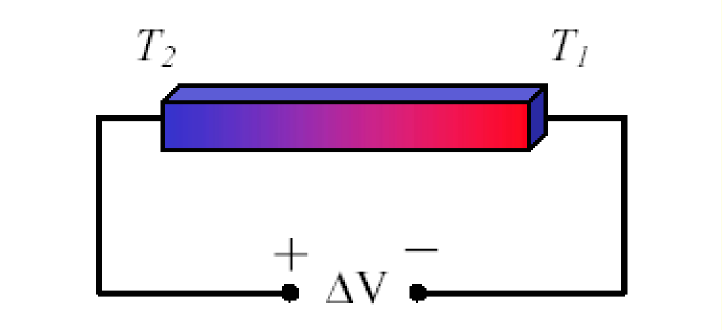
Efecto Seebeck --1821



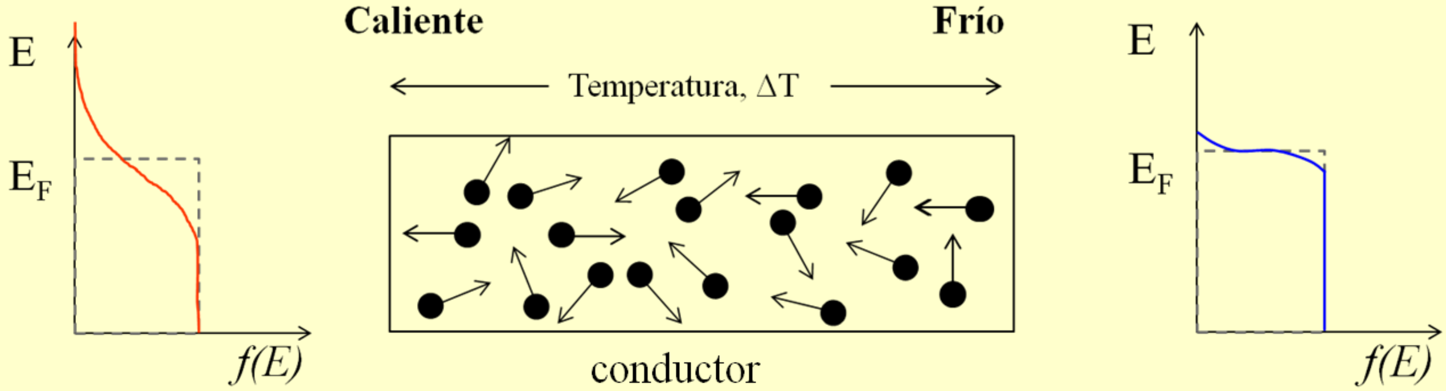
Jean Charles Peltier
1785-1845

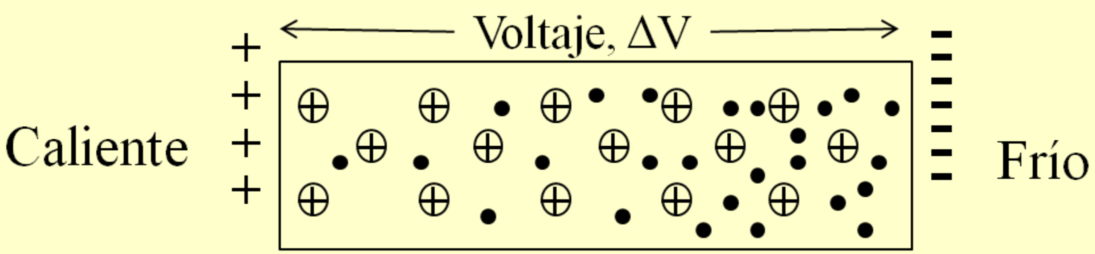
Efecto Peltier -- 1834

Efecto Seebeck



un ΔT a lo largo de una barra metálica
produce un ΔV estacionario
en condiciones de circuito abierto.
Este voltaje se denomina Voltaje Seebeck

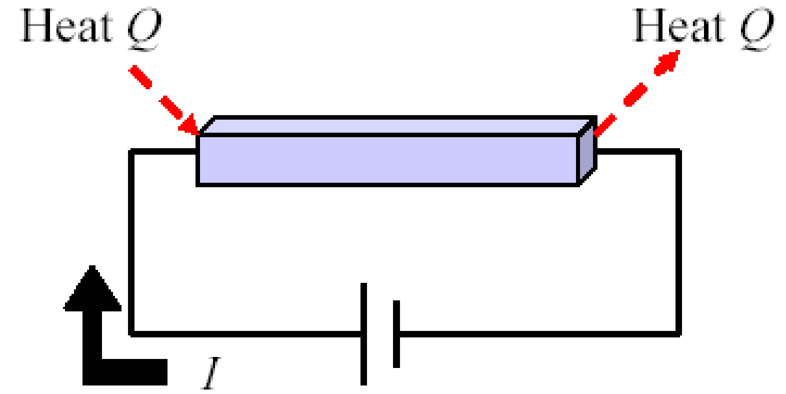




$$S = -\frac{\Delta V}{T_2 - T_1}; \quad S > 0 \quad tipo - p \quad y \quad S < 0 \; tipo - n$$

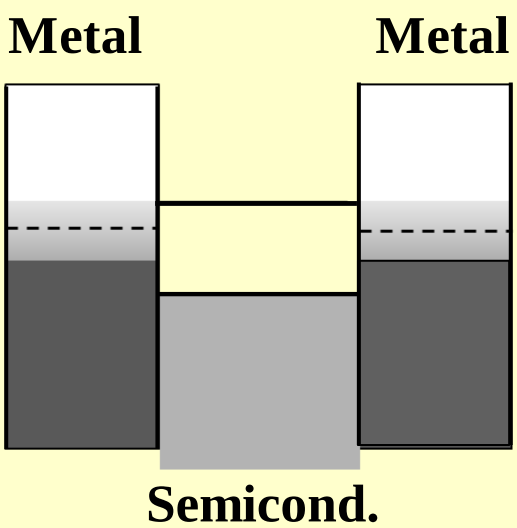
Efecto Peltier

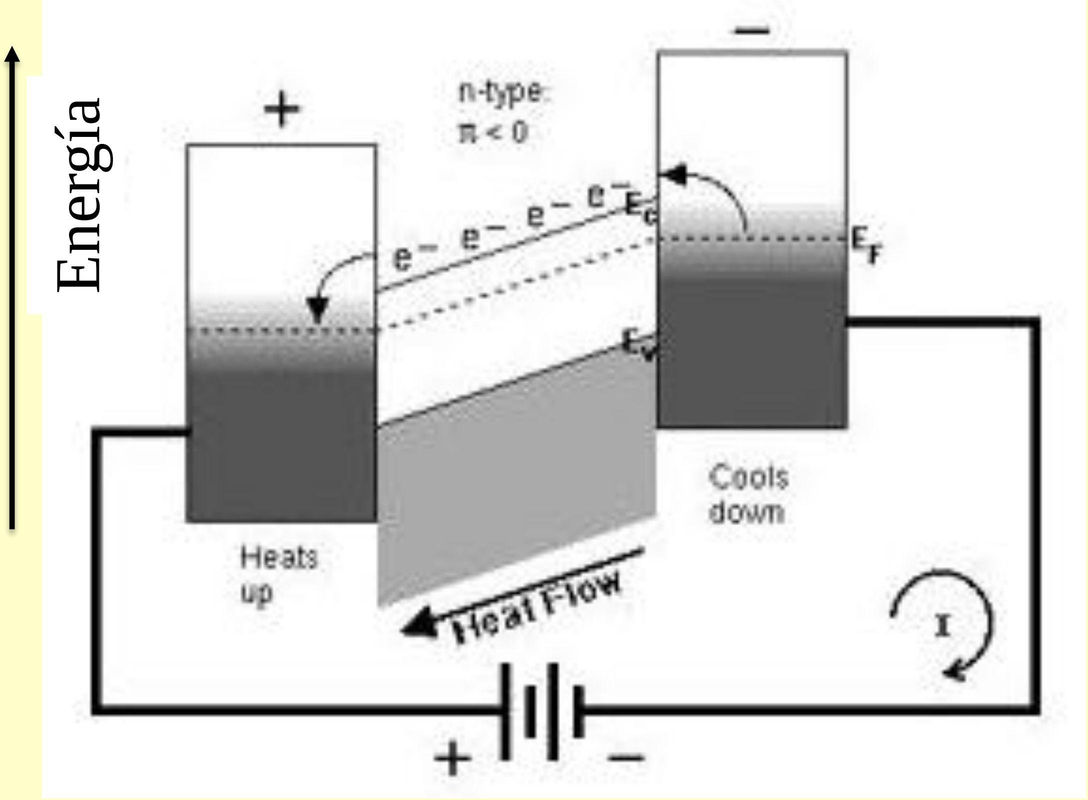
Cuando circula una corriente por una barra se crea una ΔT entre los extremos de la barra

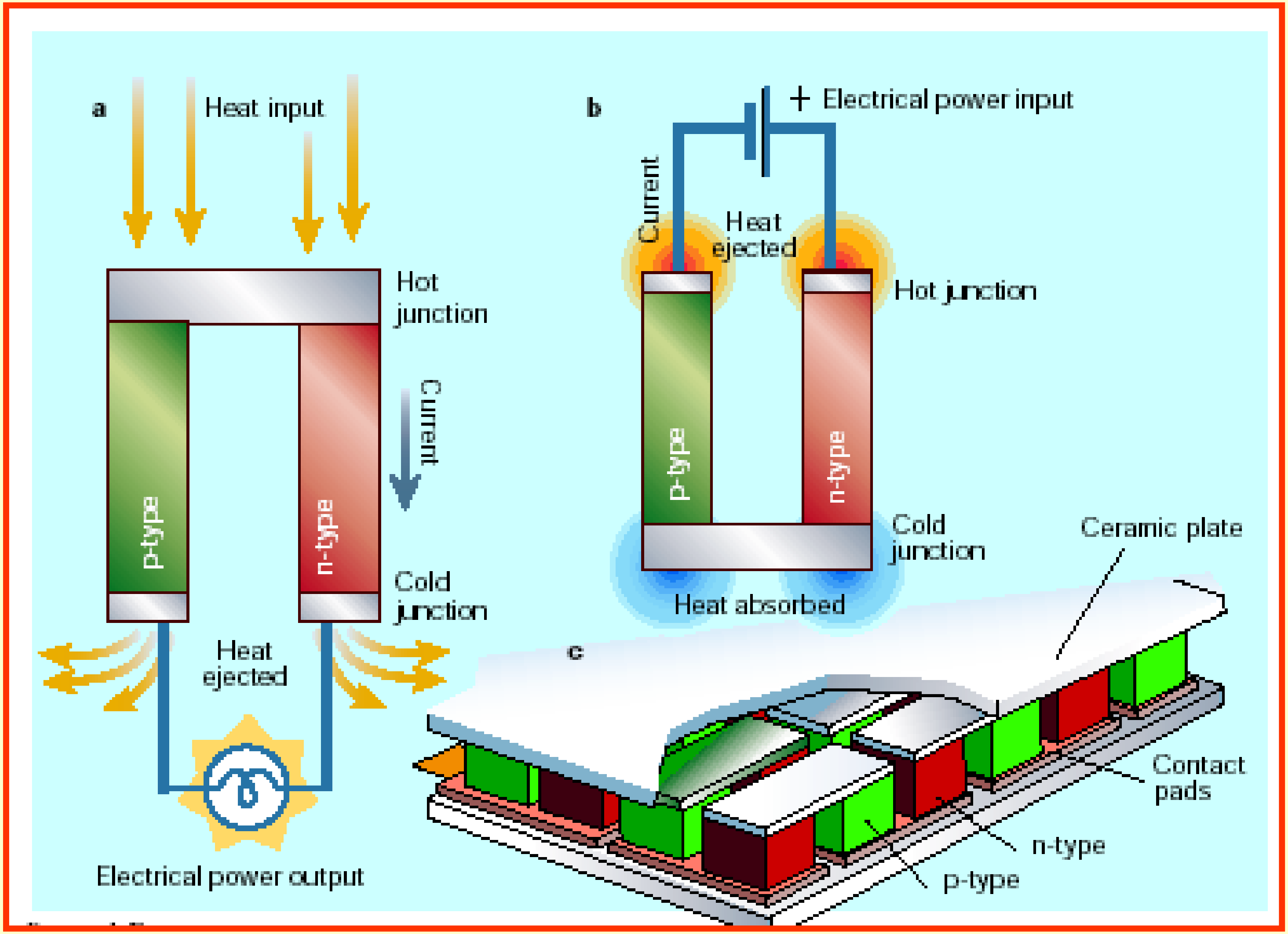


Coeficiente Peltier

$$\Pi = Q / I$$

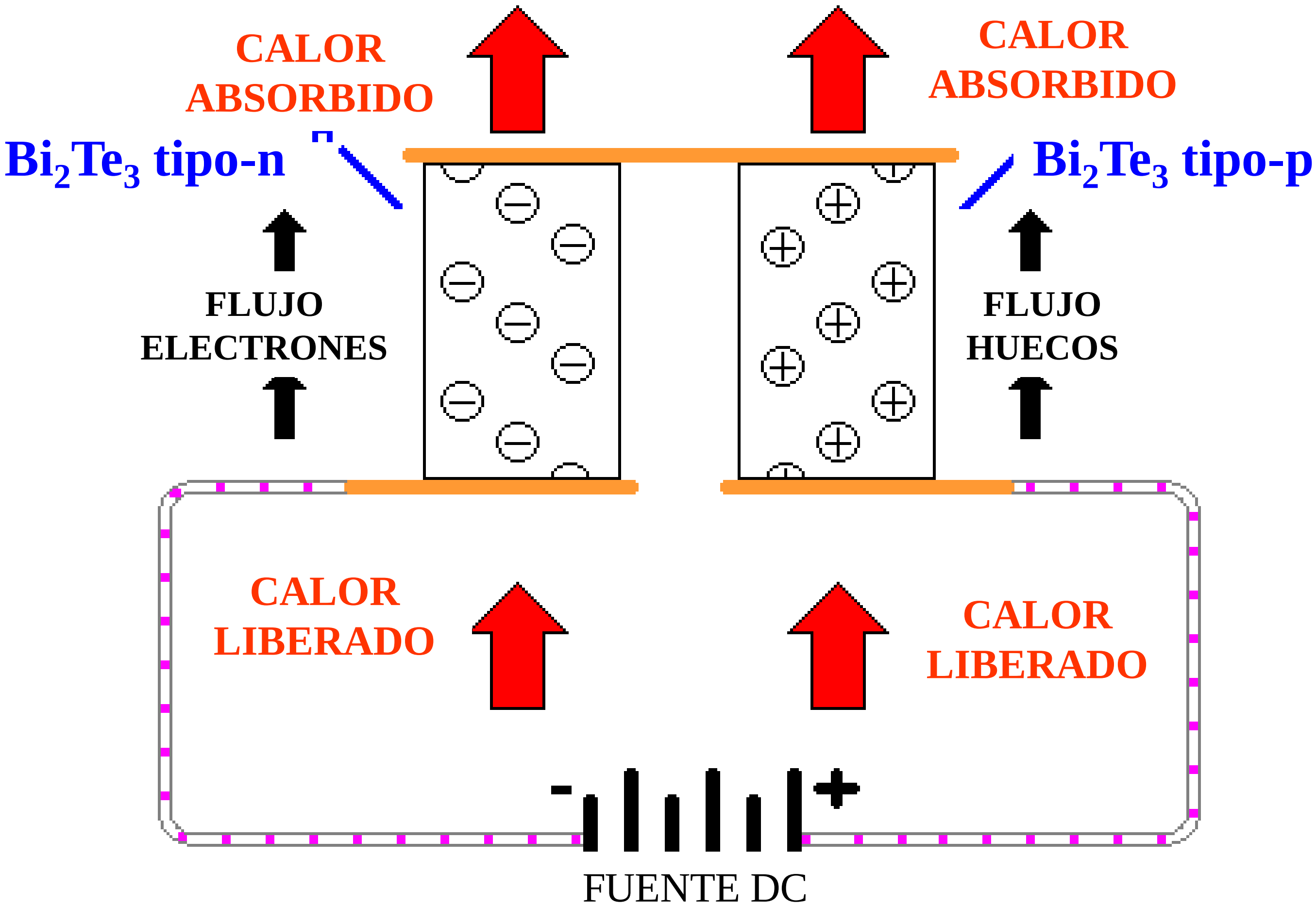






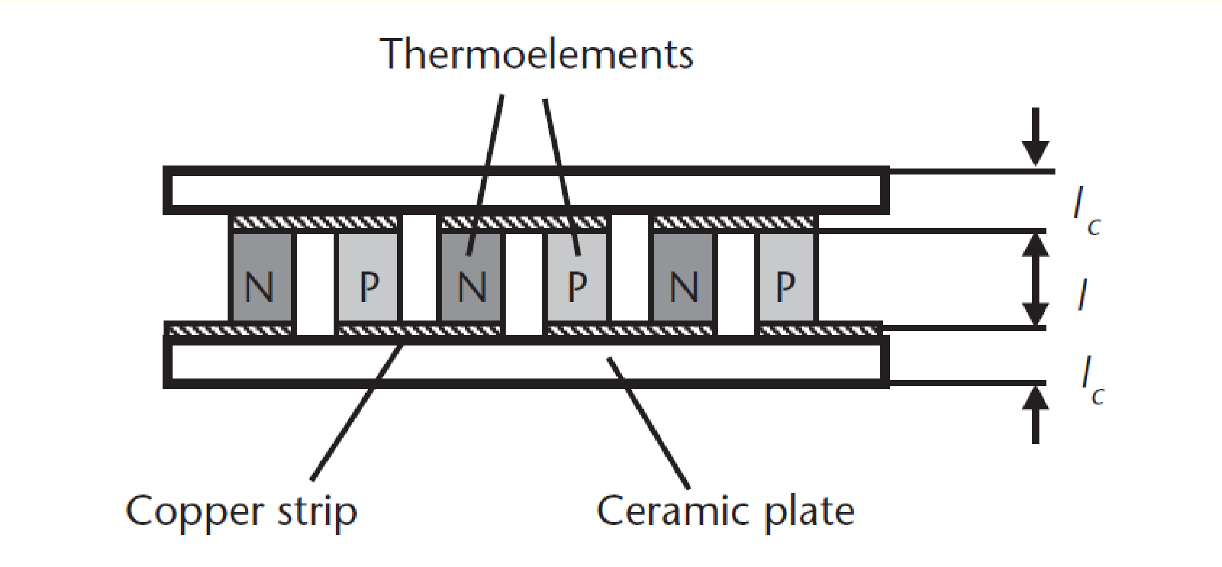
C.B.Vining, Nature, October 2001

DISPOSITIVO PELTIER



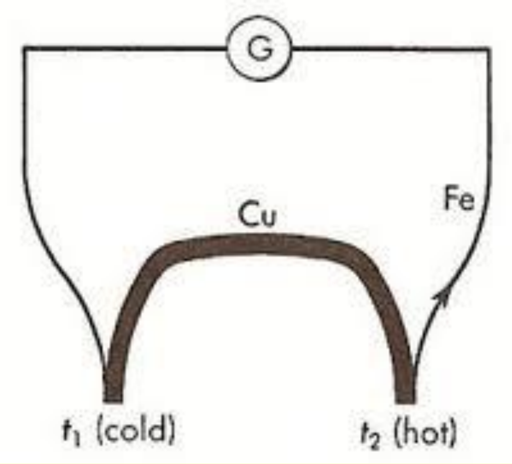
LOS PORTADORES DE CARGA, ELECTRONES NEGATIVA Y HUECOS POSITIVA, TRANSPORTAN EL CALOR

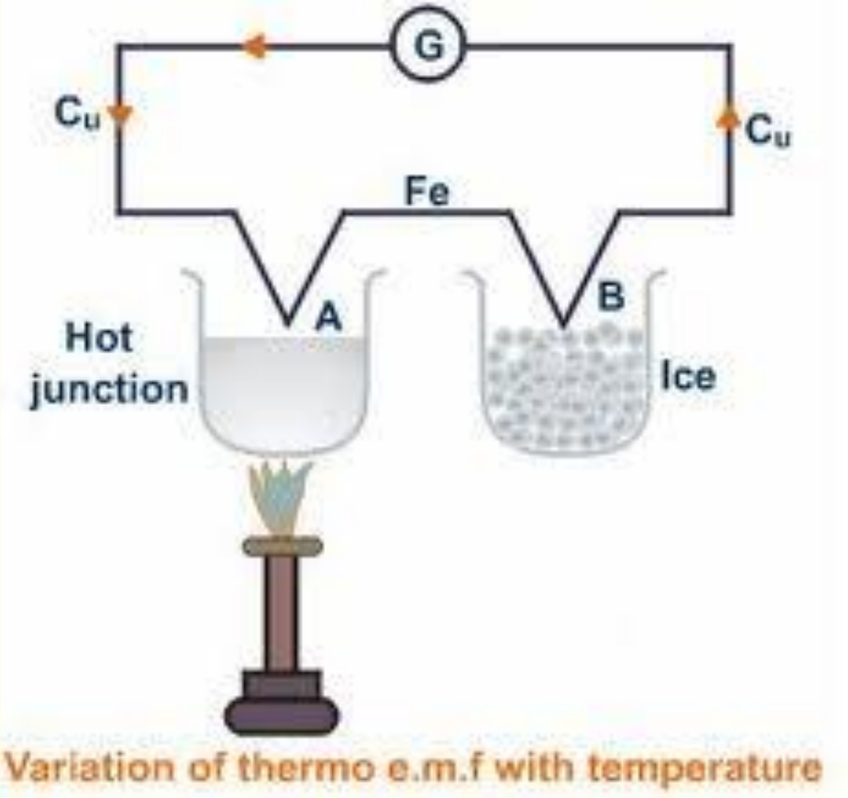
Materiales termoeléctricos



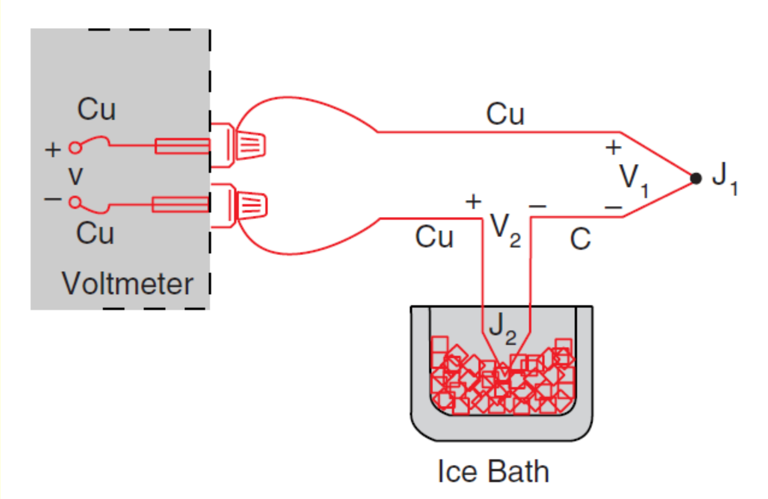
Termopares

Uniones de dos metales





$$V_{Seebeck} = (S_A - S_B) \cdot \Delta T$$



S_{Fe}=19 μV/ºC
S_{Cu}=1,8 μV/ºC
$S_{Constantan}$=-35 μV/ºC

ΔT=50ºC

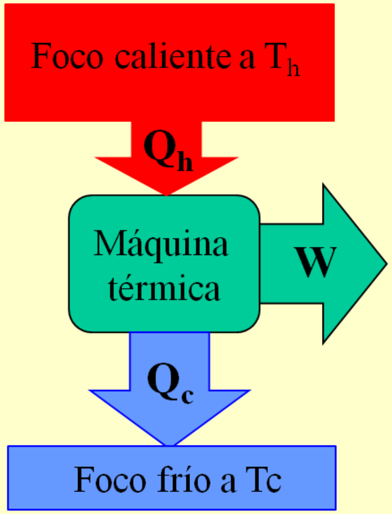
500 termopares para generar 10 V !!!

Semiconductores: los campeones de la Termoelectricidad

Metals	Seebeck Coefficient
	μV/K
Antimony	47
Nichrome	25
Molybdenum	10
Cadmium	7.5
Tungsten	7.5
Gold	6.5
Silver	6.5
Copper	6.5
Rhodium	6.0
Tantalum	4.5
Lead	4.0
Aluminum	3.5
Carbon	3.0
Mercury	0.6
Platinum	0
Sodium	-2.0
Potassium	-9.0
Nickel	-15
Constantan	-35
Bismuth	-72

Semiconductors	Seebeck Coefficient
	μV/K
Se	900
Te	500
Si	440
Ge	300
n-type Bi_2Te_3	-230
p-type $Bi_{2-x}Sb_xTe_3$	300
p-type Sb_2Te_3	185
PbTe	-180
$Pb_{03}Ge_{39}Se_{58}$	1670
$Pb_{06}Ge_{36}Se_{58}$	1410
$Pb_{09}Ge_{33}Se_{58}$	-1360
$Pb_{13}Ge_{29}Se_{58}$	-1710
$Pb_{15}Ge_{37}Se_{58}$	-1990
$SnSb_4Te_7$	25
$SnBi_4Te_7$	120
$SnBi_3Sb_1Te_7$	151
$SnBi_{2.5}Sb_{1.5}Te_7$	110
$SnBi_2Sb_2Te_7$	90
$PbBi_4Te_7$	-53

Eficiencia termoeléctrica



Eficiencia de una máquina térmica

$$\eta = \frac{E_{\text{suministrada}}}{E_{\text{producida}}} = \frac{E_{entrada}}{E_{salida}} \qquad \eta = \left(\frac{T_h - T_c}{T_h}\right)$$

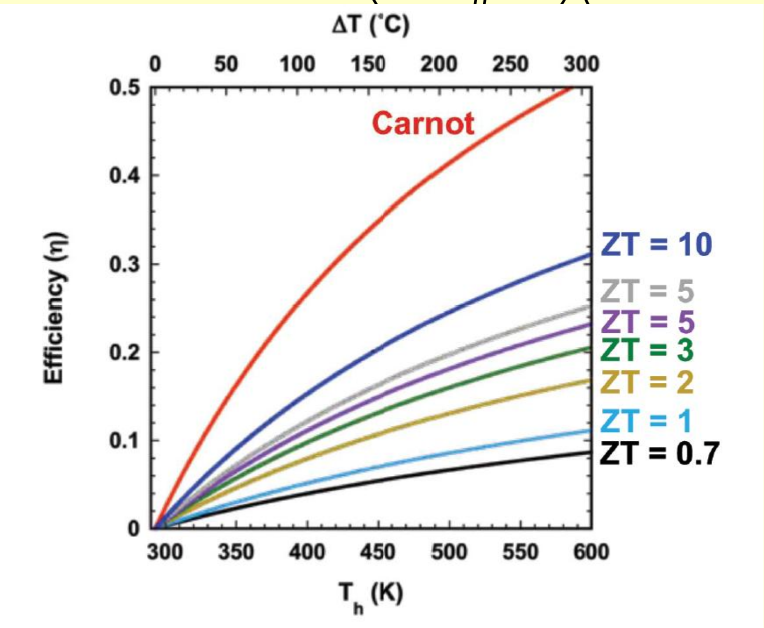
Eficiencia termoeléctrica

$$\eta = \left(\frac{T_h - T_c}{T_h}\right)\left(\frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+T_c/T_h}\right) \quad ;$$

Figura de mérito

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

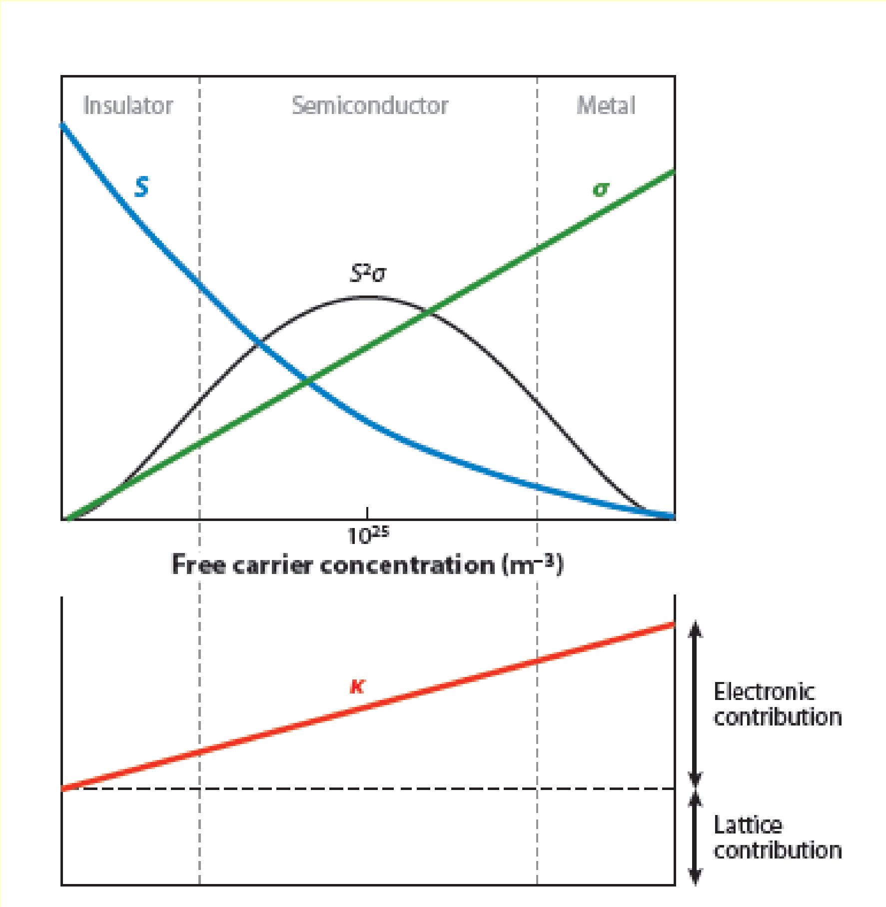
Power factor

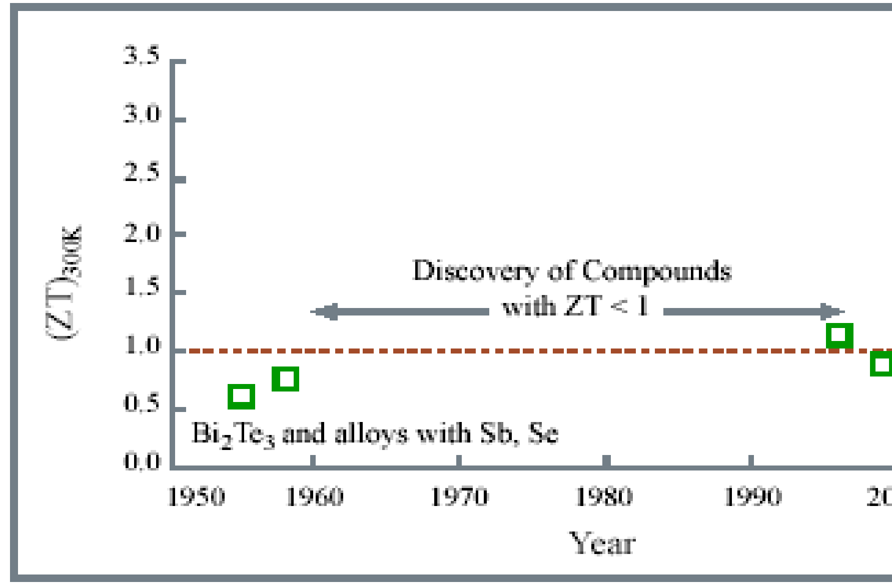


κ conductividad térmica
σ conductividad electrica
S Coeficiente Seebeck

ZT=1 -- ΔT=500 K, η= 12%
ZT=2 -- ΔT=500 K, η= 22%

$$Z = \frac{S^2\sigma}{\kappa}$$





ZT ~ 1 (BiTe) today

Ley de Wiedemann-Franz $$\frac{k}{\sigma} = \frac{3}{2}\left(\frac{k_B}{e}\right)^2 T \quad \longrightarrow$$

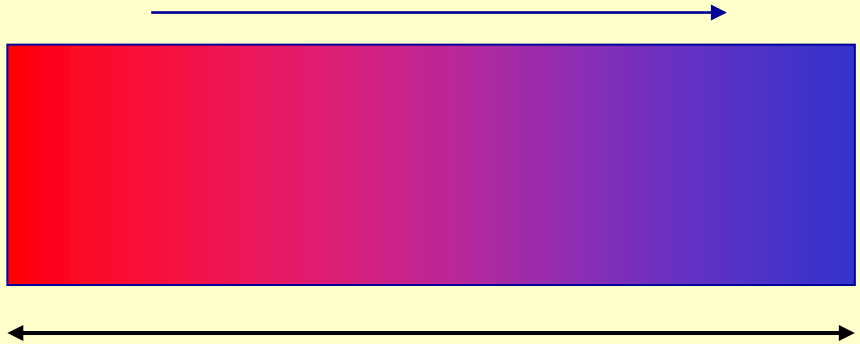
$S \uparrow \;\Rightarrow\; \sigma \uparrow$

$\sigma \uparrow \;\Rightarrow\; \kappa \uparrow$

Ley de Fourier: Conducción Térmica

Q **(flujo de calor)**

Caliente
T_h



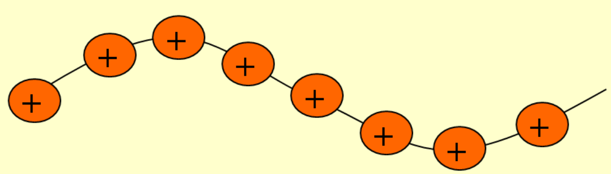
Frío
T_c

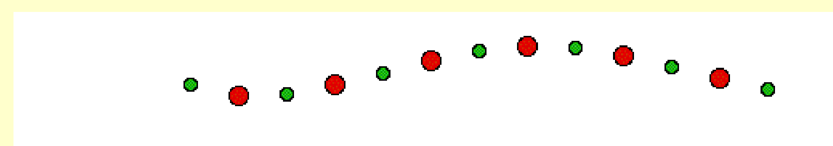
L

$$Q = kA\frac{T_h - T_c}{L} = kA\frac{dT}{dx}$$

Conductividad térmica

Onda Acústica

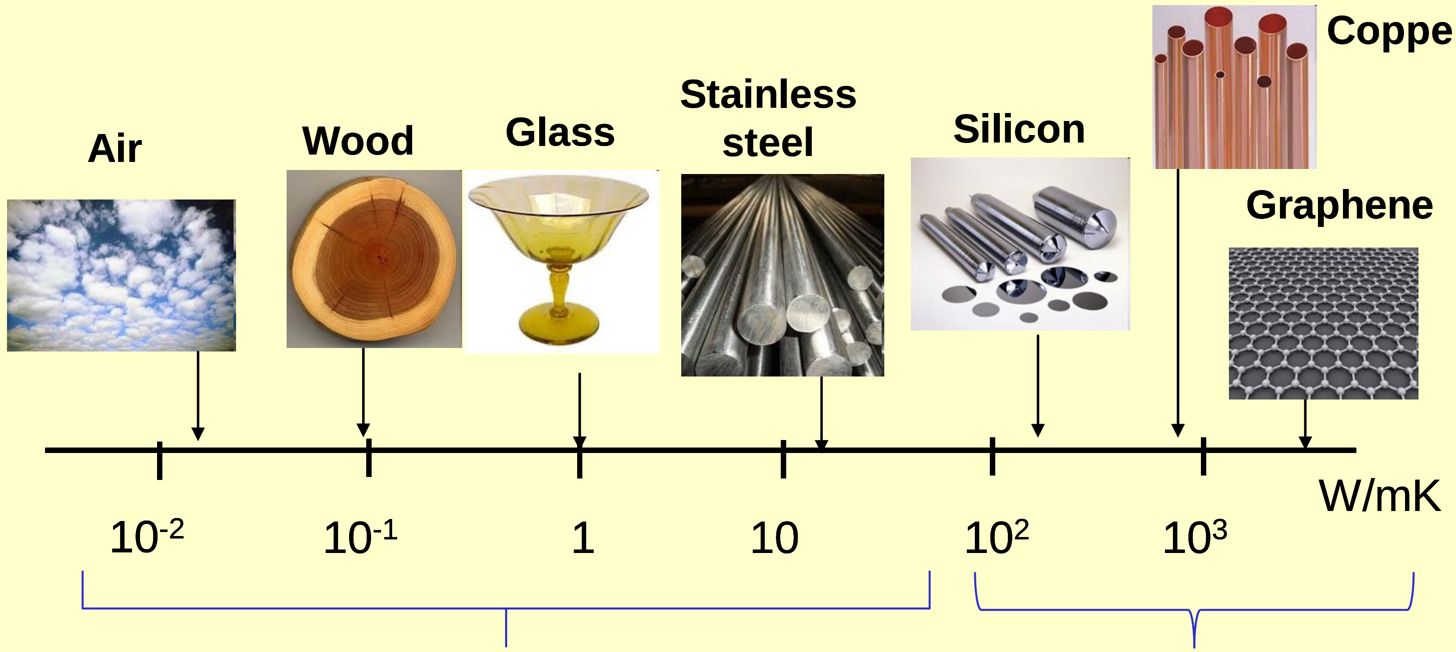




$$Z = \frac{S^2\sigma}{\kappa}$$

Conductividad Térmica

Material



Transferencia de energía → **vibraciones atómicas** | **vibraciones atómicas movimiento de electrones**

Phonon Glass --- Electron Conductor
Vidrio de fonones --- Conductor de electrones

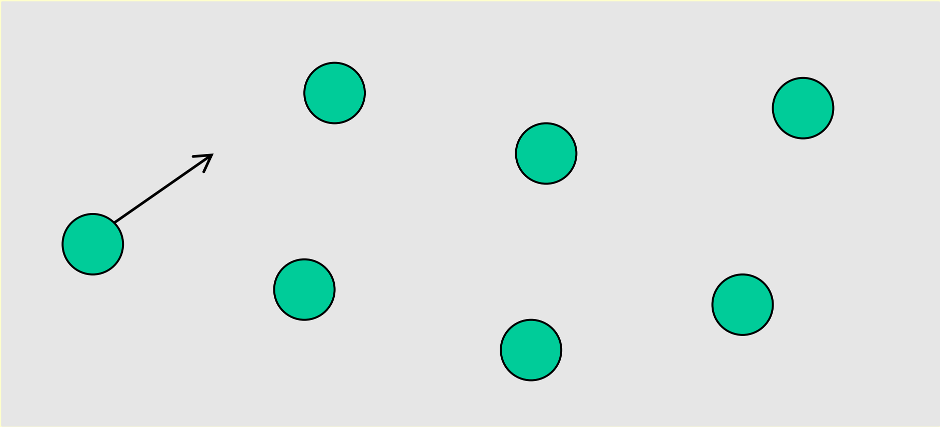
Conductividad Térmica

$$k_l = \frac{1}{3} C_l \cdot v_s \cdot \ell_l$$

C_l -- Capacidad calorífica
v_s -- velocidad del sonido
ℓ_l -- recorrido libre medio

Recorrido Libre medio

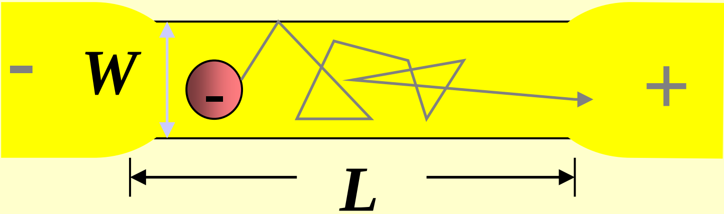
l ~ 100 nm en Si o Ge cristalino



$W \leq l$: scattering intercaras

$W \leq \lambda_F$: efectos cuánticos

$L \leq l$: transporte balístico

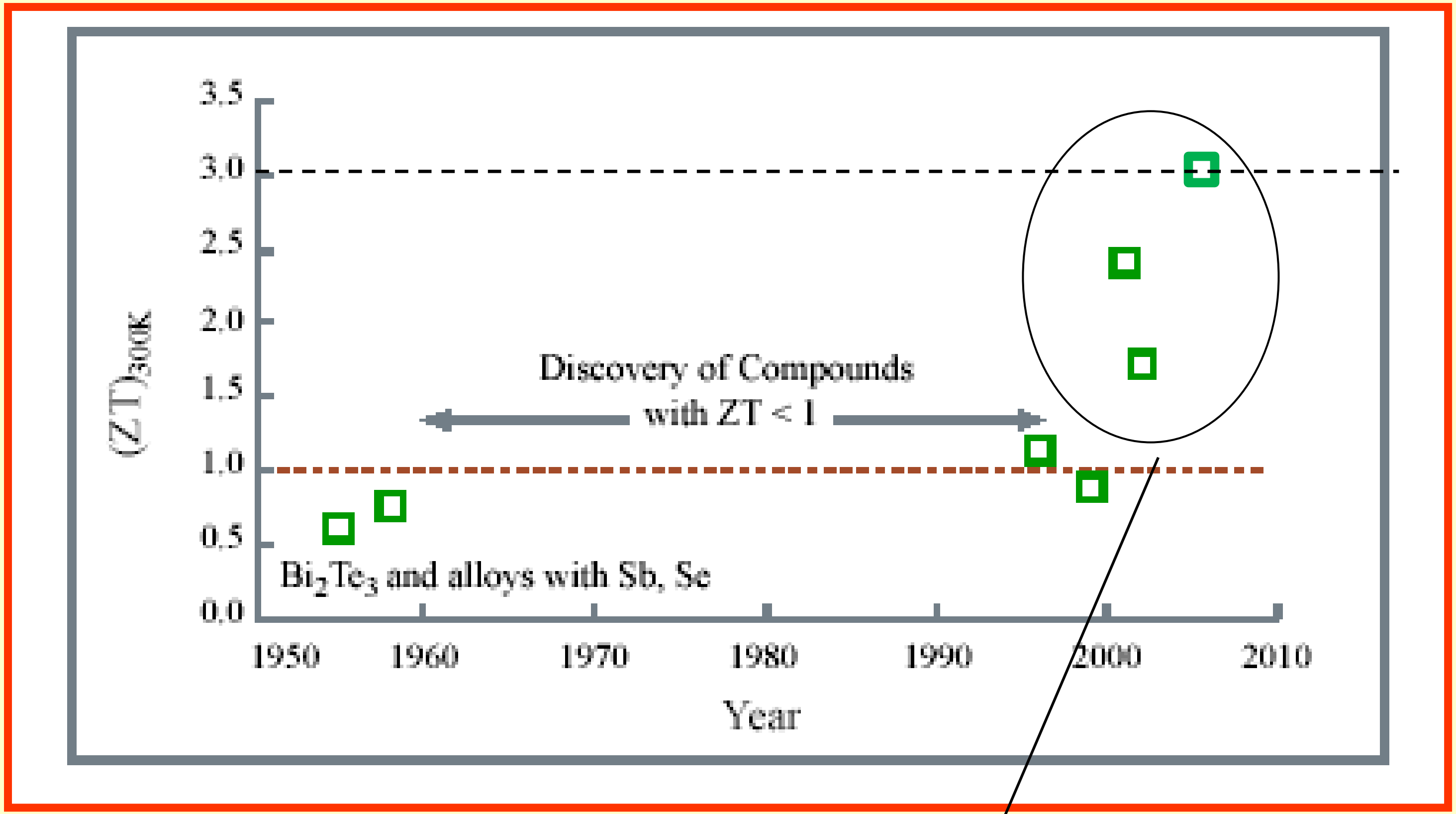


Eficiencia, eficiencia, eficiencia:

En busca del Santo Grial o Figura de mérito = 3.

$$Z = \frac{S^2\sigma}{\kappa}$$

Evolución de la Figura de Mérito (ZT)



ESTRUCTURAS (MATERIALES) DE BAJA DIMENSIONALIDAD

Nanomateriales

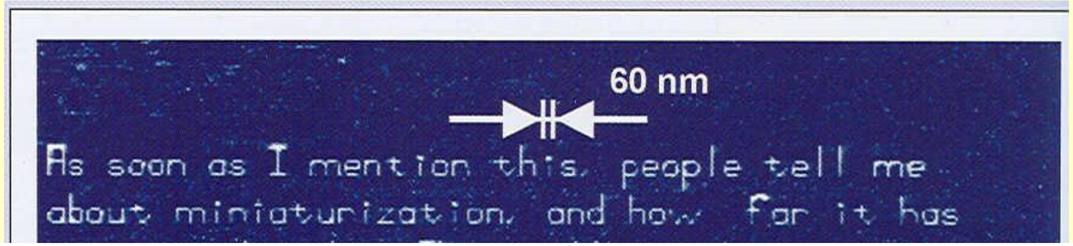
Materiales con tamaños en alguna dimensión del orden de 1 a 100 nm

El nacimiento de la Nanotecnología

MINIATURIZACIÓN

Richard Feynman

“There is plenty of room at the bottom”, 1959



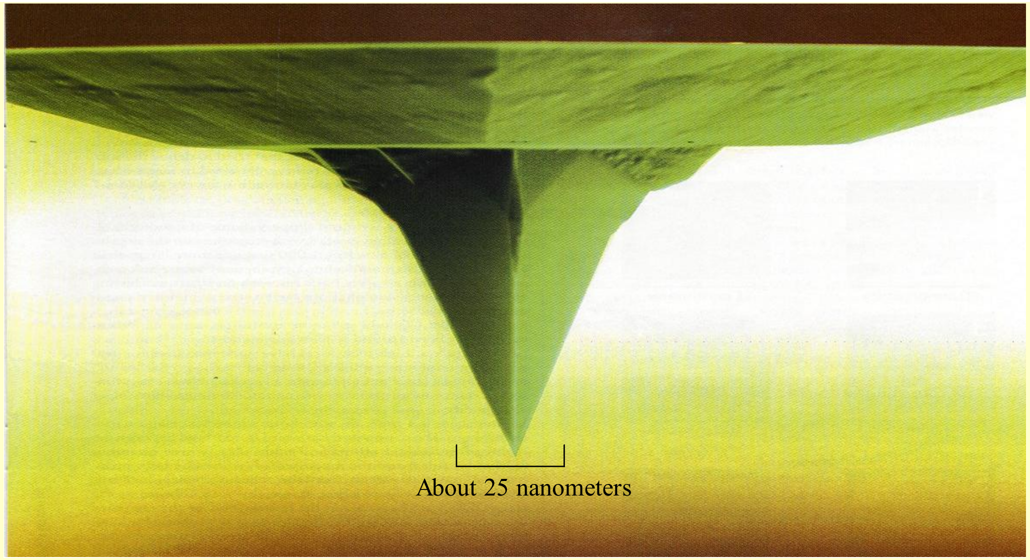
What I want to talk about is the problem of manipulating and controlling things on a small scale.

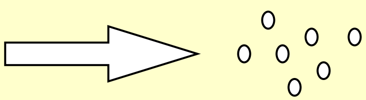
Why cannot we write the entire 24 volumes of the Encyclopedia Brittanica on the head of a pin?

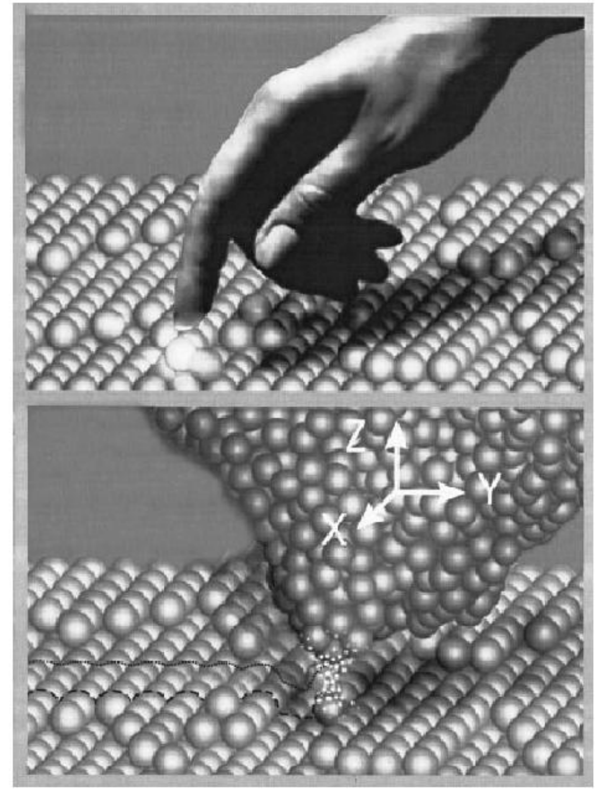
Perhaps this doesn't excite you to do it, and only economics will do so. Then I want to do something; but I can't do it at the present moment, because I haven't prepared the ground. It is my intention to offer a prize of $1,000 to the first guy who can take the information on the page of a book and put it on an area 1/25,000 smaller in linear scale in such manner that it can be read by an electron microscope.
And I want to offer another prize---if I can figure out how to phrase it so that I don't get into a mess of arguments about definitions---of another $1,000 to the first guy who makes an operating electric motor---a rotating electric motor which can be controlled from the outside and, not counting the lead-in wires, is only 1/64 inch cube.
I do not expect that such prizes will have to wait very long for claimants.

Figure 4.1
The founding speech of nanotechnology—written at the nanoscale.
Courtesy of the Mirkin Group, Northwestern University.

Microscopías de sonda





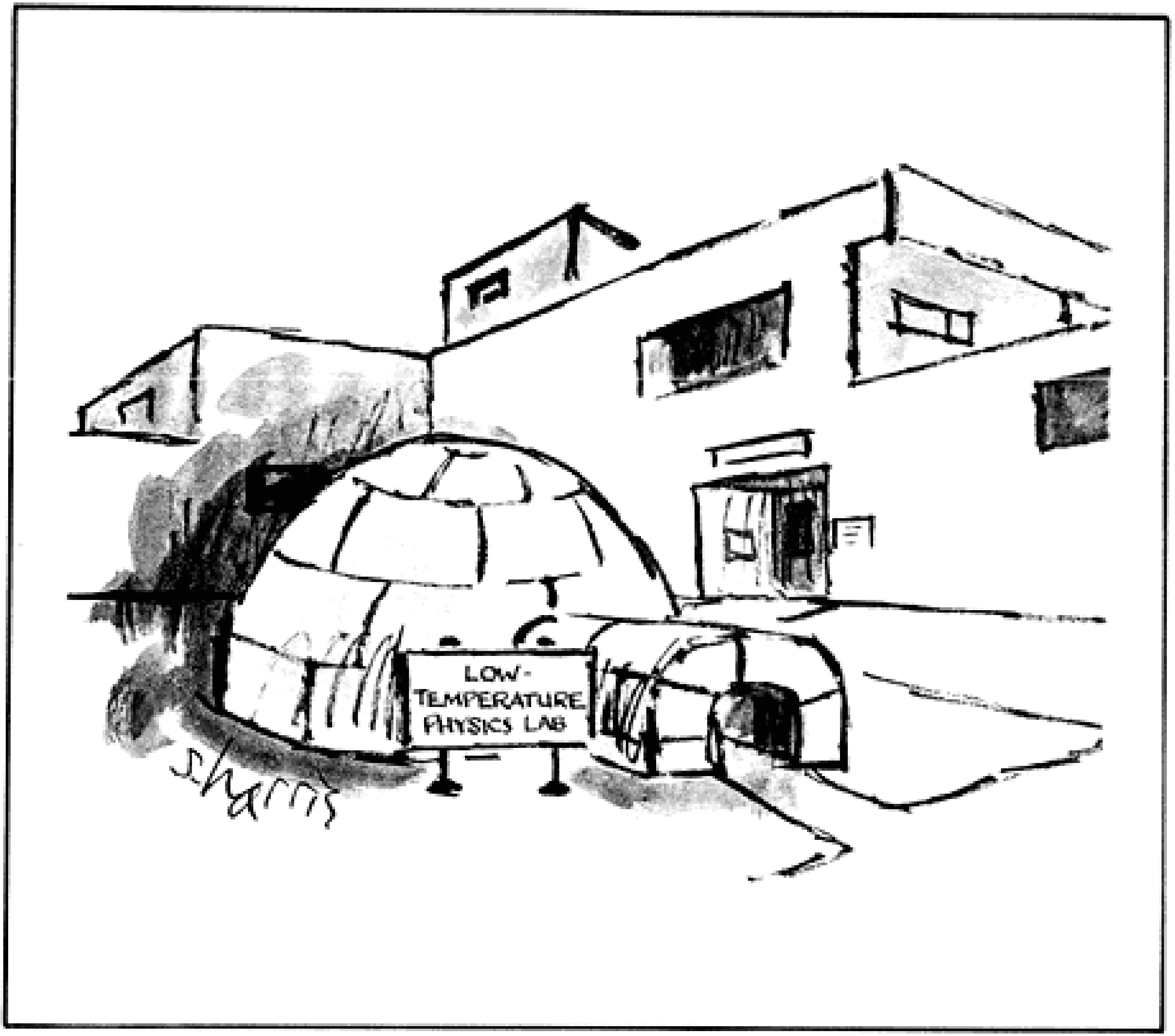


Microscopies d'escombrat amb sonda local

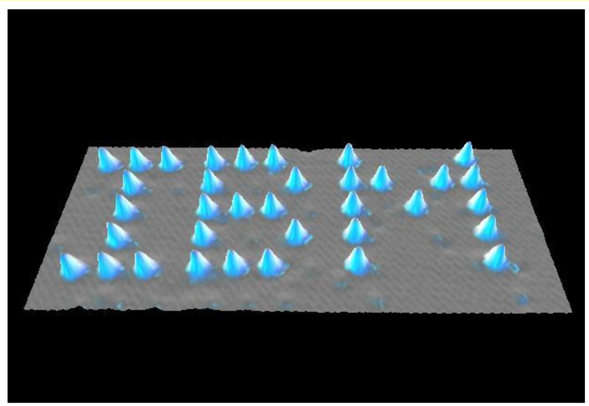
(SPM: scanning probe microscopes)

The Nobel Prize in Physics 1986

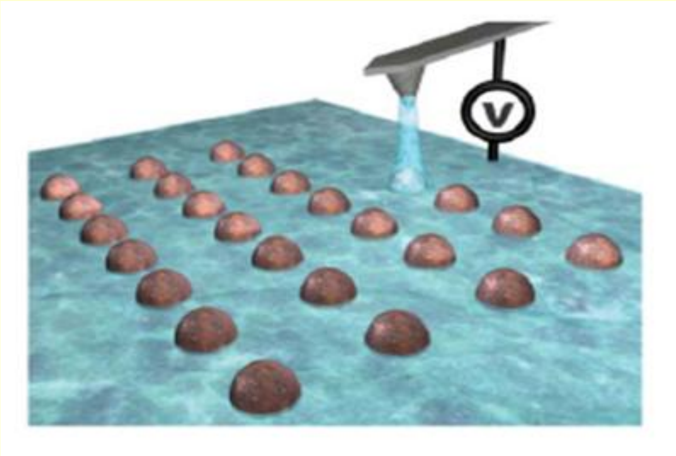
Gerd Binnig **Heinrich Rohrer**

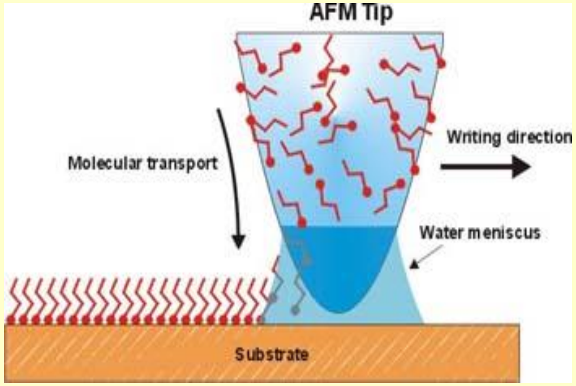

LOW-
TEMPERATURE
PHYSICS LAB
S.Harris

Nanofabricación (bottom-up)



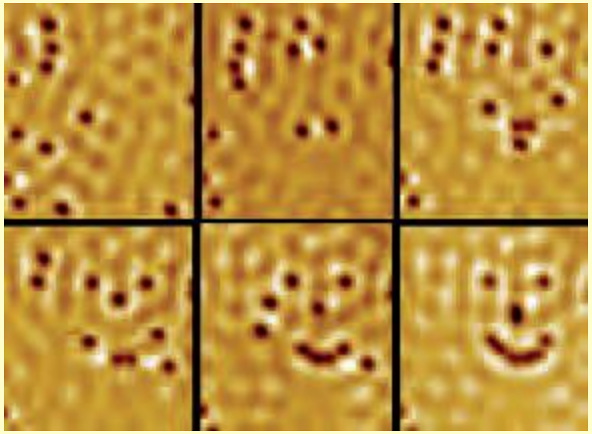
Átomos de Xe sobre superficie de Ni



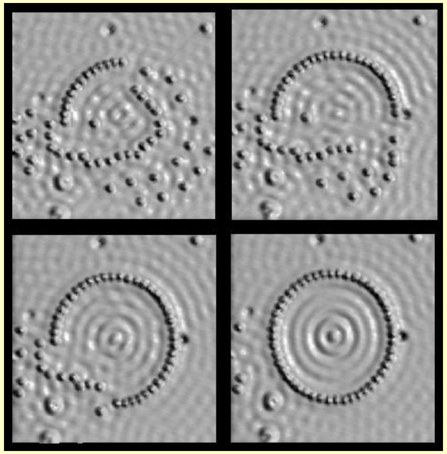


Transporting molecules to a surface by dip-pen nanolithography

Nanosonrisa
con moléculas de CO



R. Miranda, IMDEA nanociencia , Madrid



SÍNTESIS DE MATERIALES EN LA NANOESCALA

PROCESADO de MATERIALES

Bottom-up vs. Top-down

<u>Procesado Top-down</u>

Remover material hasta obtener el producto deseado

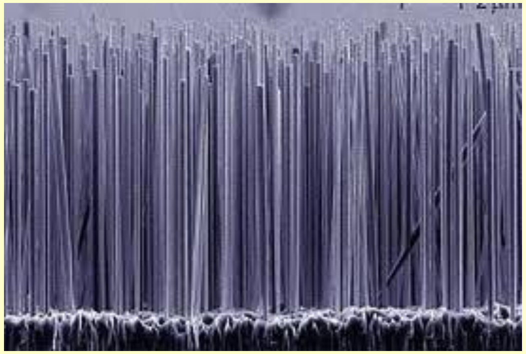
<u>Procesado Bottom-up</u>

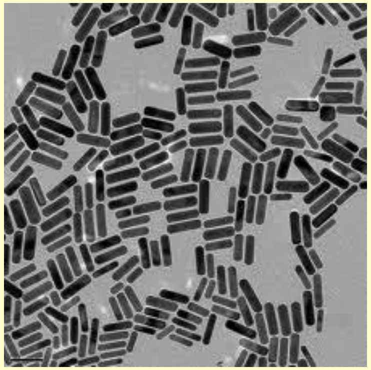
Añadir material hasta crear el producto final

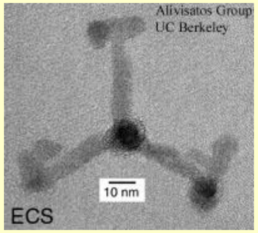
SÍNTESIS de MATERIALES en la NANOESCALA (Bottom-up)

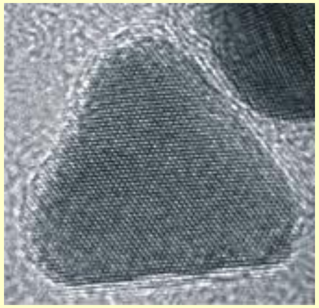
Objetos 3D, 2D, 1D, 0D

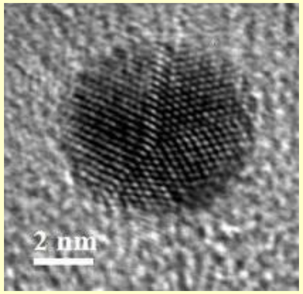
r=1,5-10 nm
200-10.000 átomos

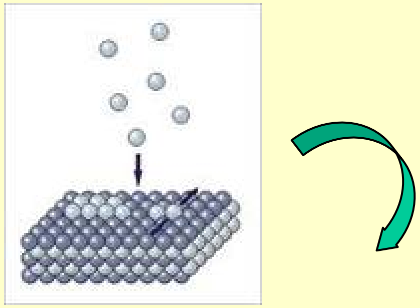


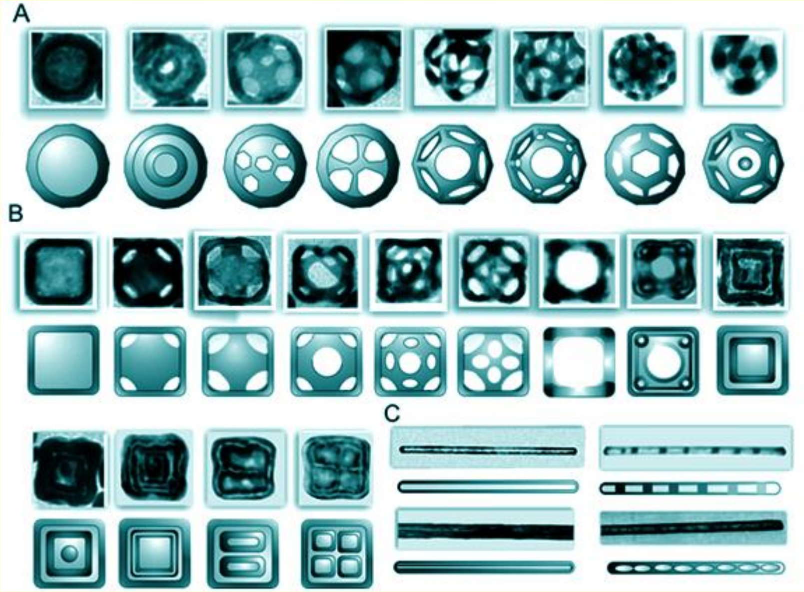




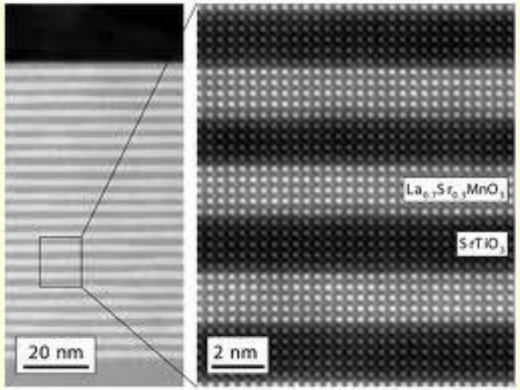


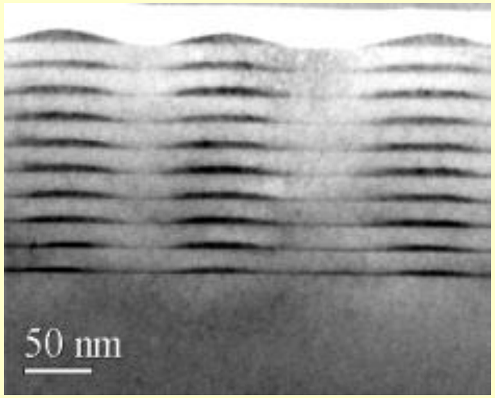




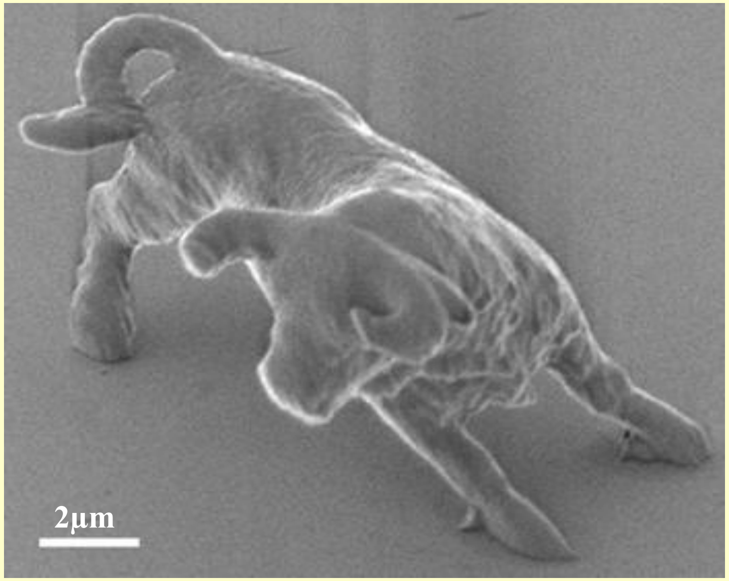


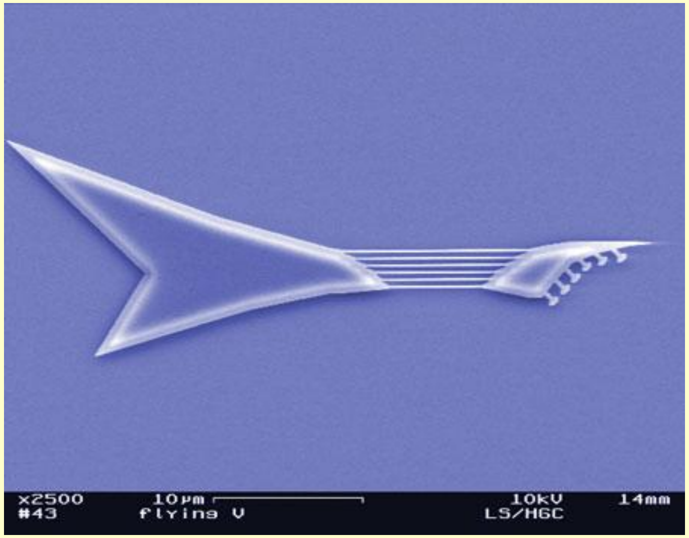
V. Puntes Group, ICN, UAB campus, Barcelona

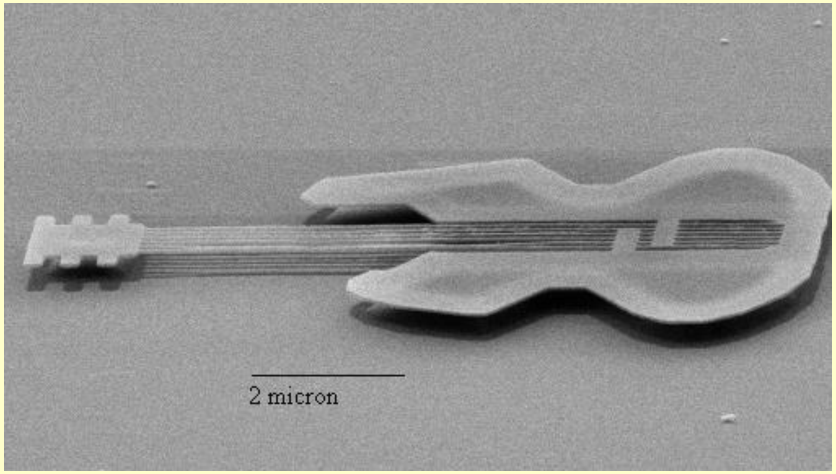


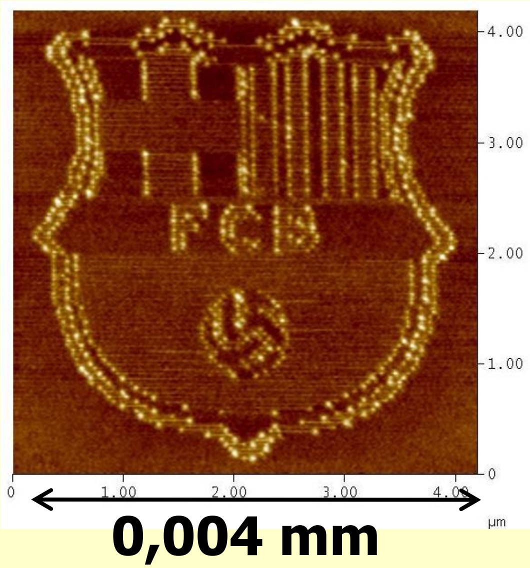


Nanofabricación (top-down)



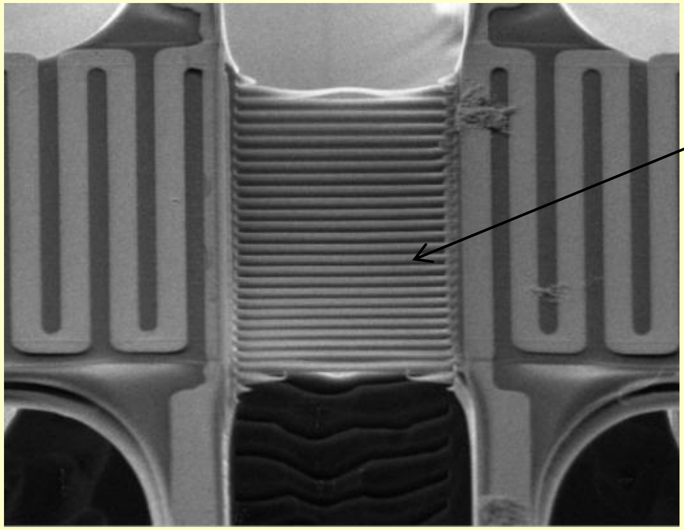


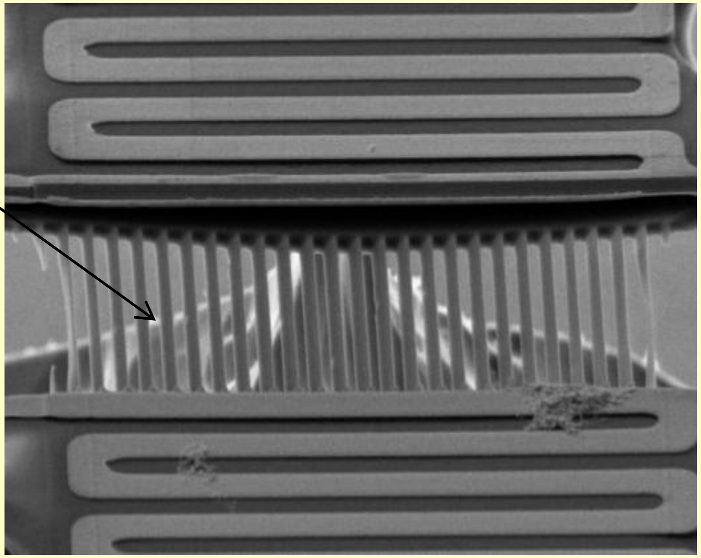


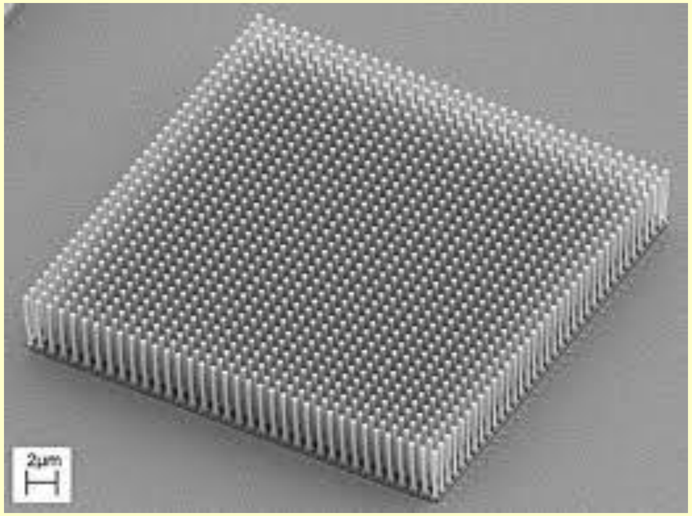


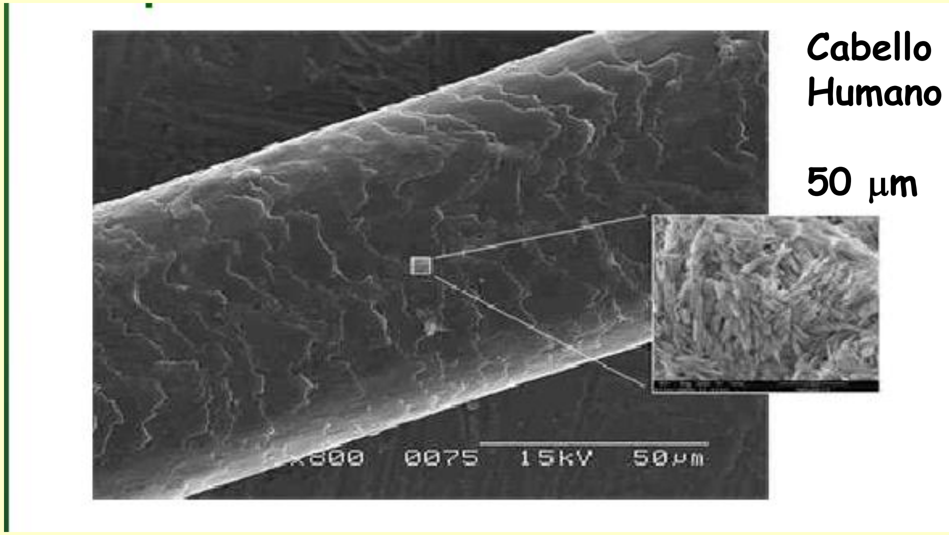
Nanohilos u otras estructuras (top-down)

~ 100 nm



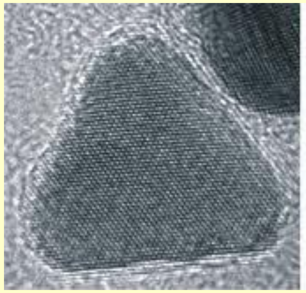


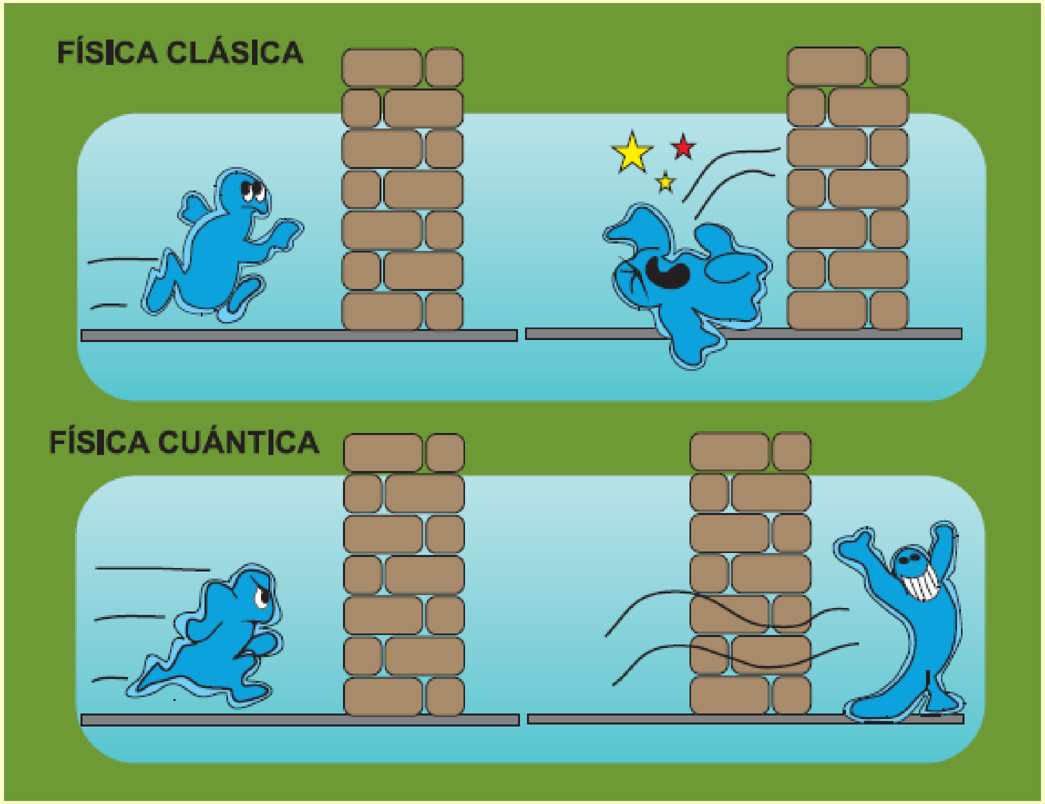




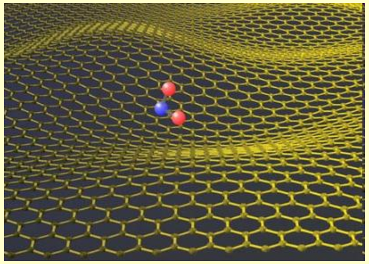
PROPIEDADES en la NANOESCALA

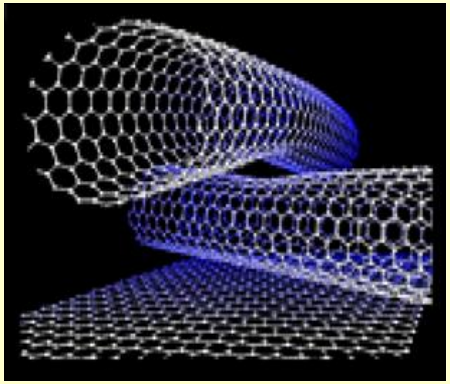
LA CAJA de las SORPRESAS





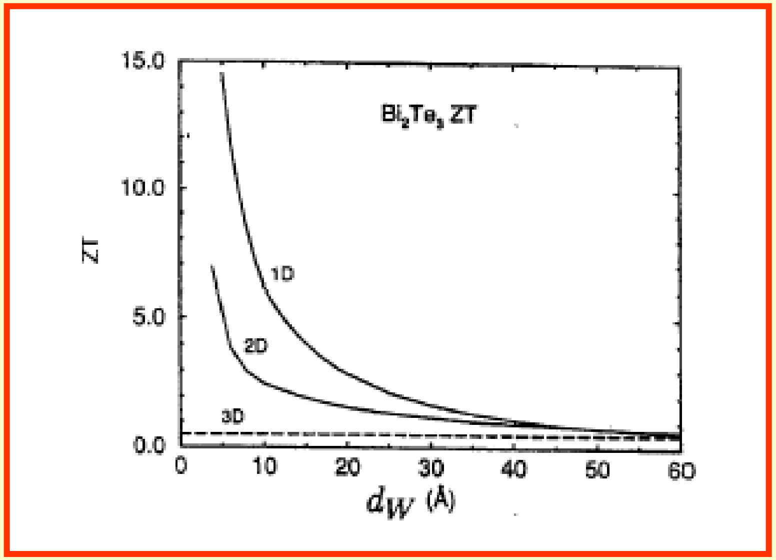
Dibujo de FECYT

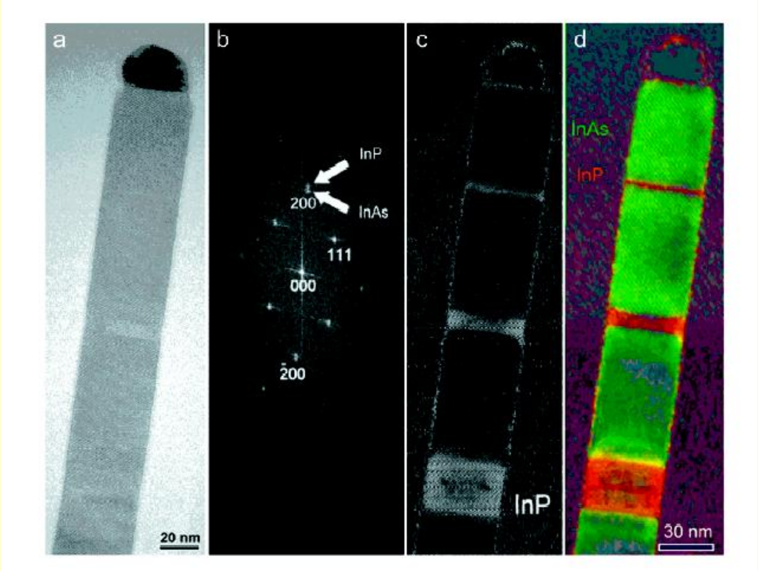




PREDICCIONES TEÓRICAS
(Dresselhaus, PRB 2002)

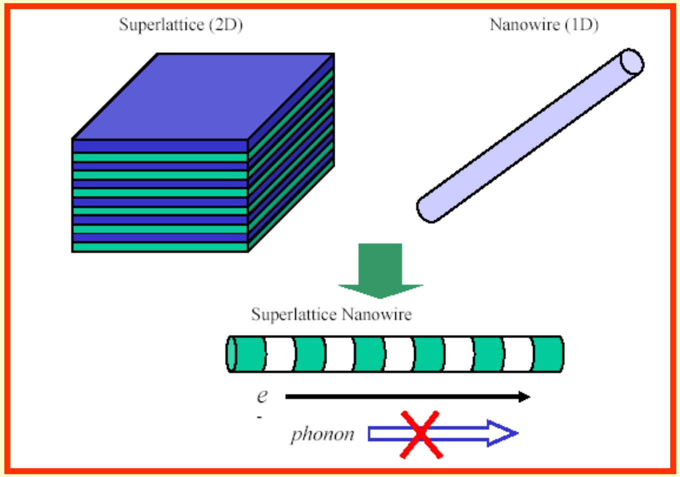
Influencia de la dimensionalidad en la figura de mérito





Realización experimental

Reduciendo la dimensio-nalidad a 0D aumentará la figura de mérito.



MATERIALES QUE CONDUCEN LA ELECTRICIDAD pero no el CALOR

Caso del Silicio

Silicio 3D

$\kappa \sim 150$ W/mK
S ~ 250 μV/K
$\sigma \sim 10^5$ S/m

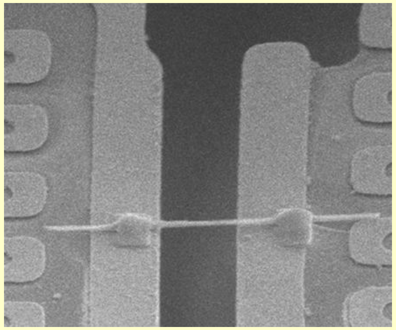
ZT = 0.01 a 300 K

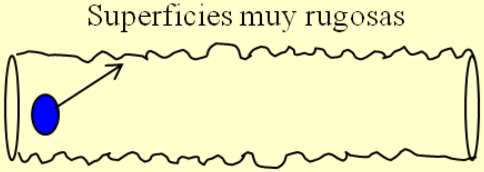
Nanohilos de Si

Silicio 1D
Nanohilo de 50 nm de diámetro

Año 2008

Heath, Nature 2008
Majumdar, Nature 2008





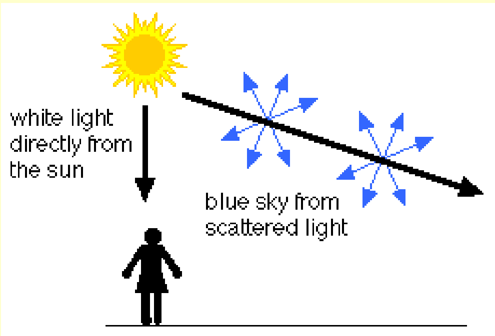
$\kappa \sim 1,60$ W/mK
S ~ 250 μV/K
$\sigma \sim 6x10^4$ S/m

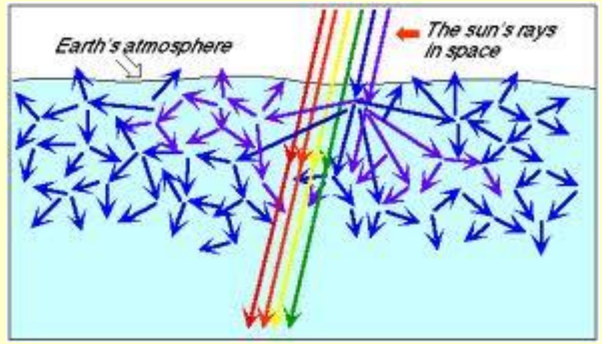
ZT ~ 1 a 300 K

Otras formas de reducir k

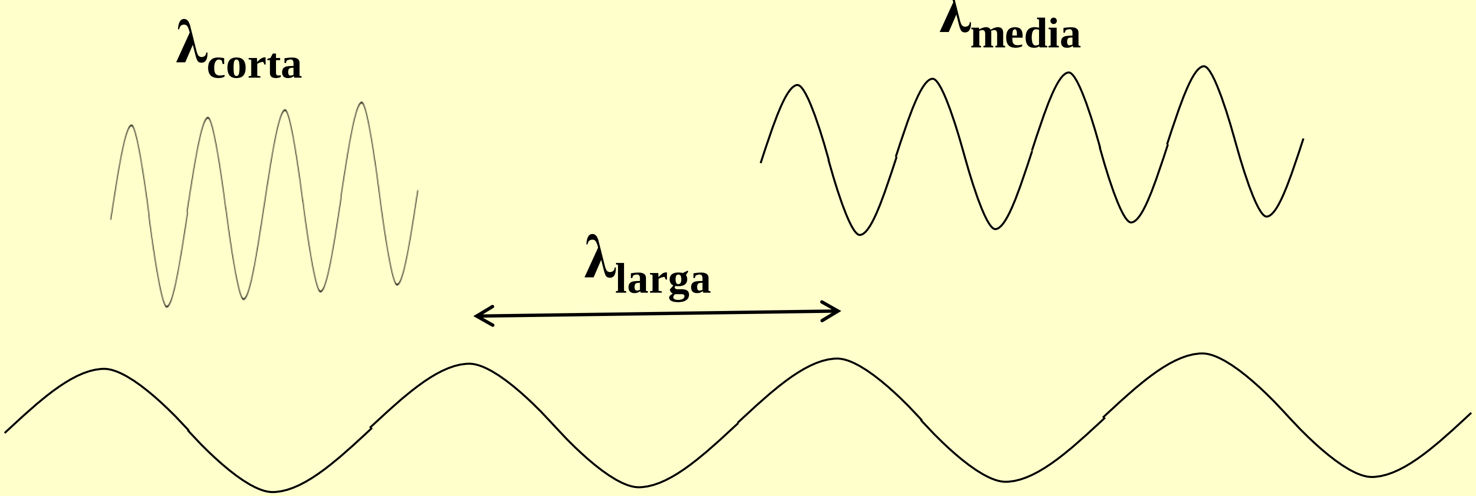
Dispersión Rayleigh

Regimen de Scattering Rayleig: Sección eficaz de scattering $\sim$ b^6/λ^4



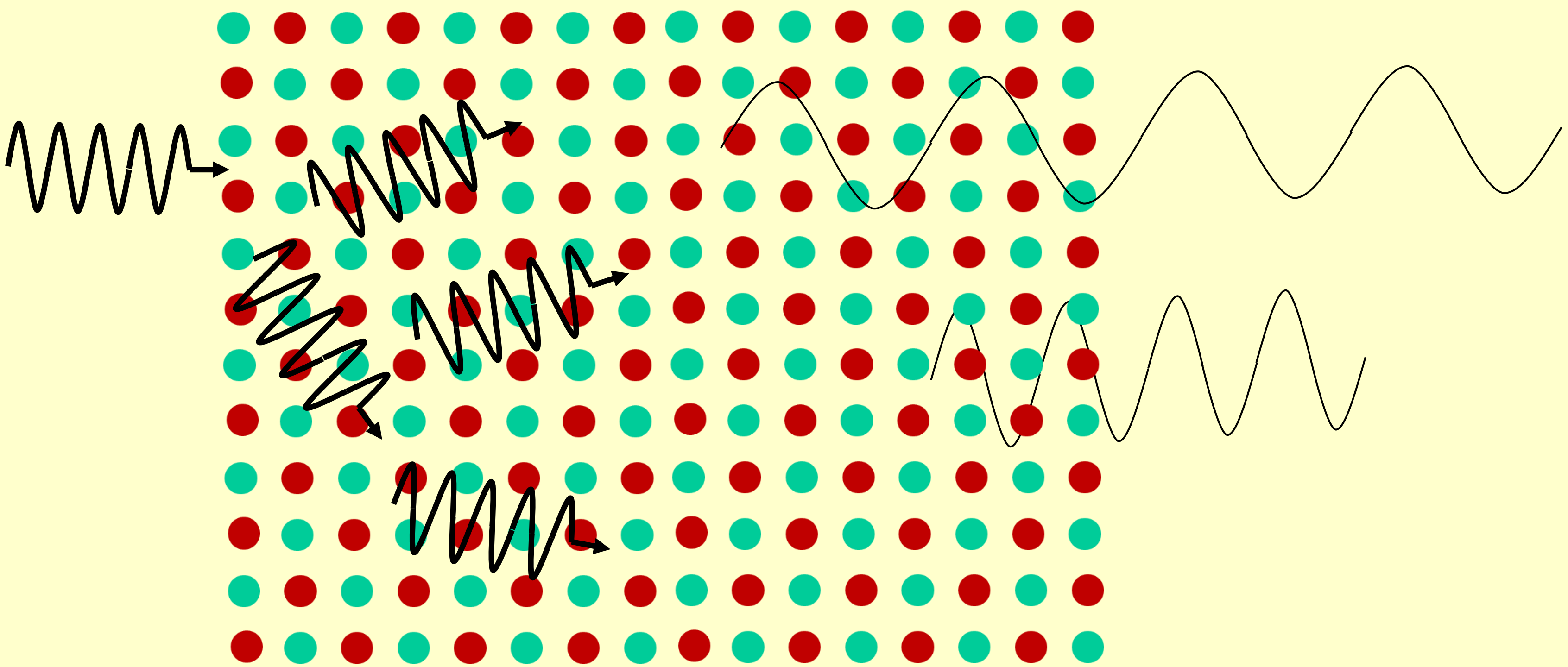


Podemos pensar en los fonones como ondas **a 300 K $\lambda_{fonon} \sim$ 1-3 nm**

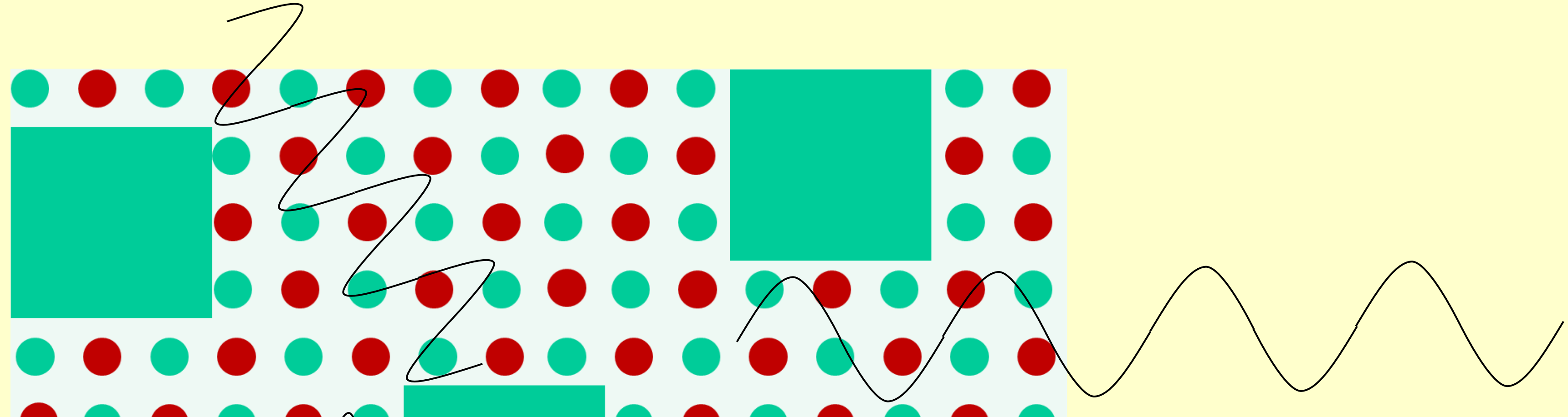


Podemos conseguir reducción:

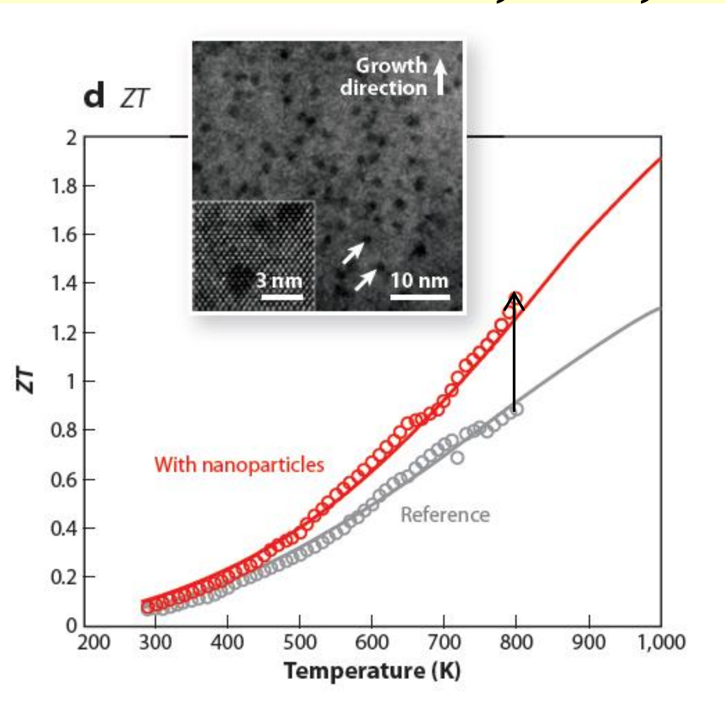
Si átomos b ~ 1Å. Las aleaciones producirán scattering de fonones con longitudes de onda cortas



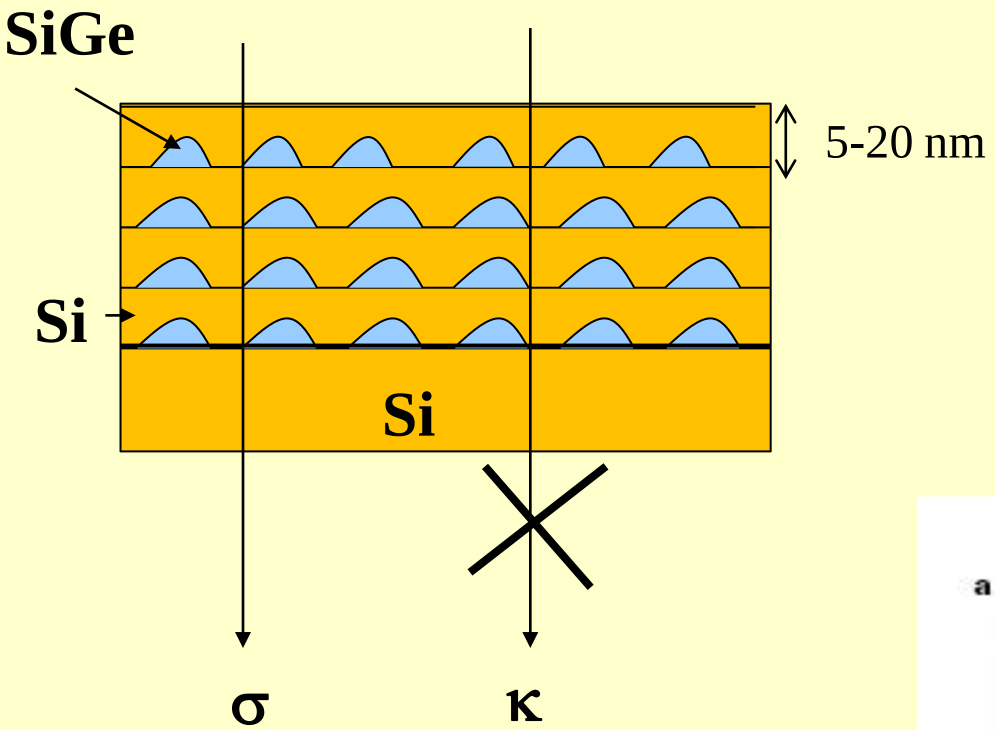
Nanopartículas de 5 nm de ErAs en una matriz de InGaAs



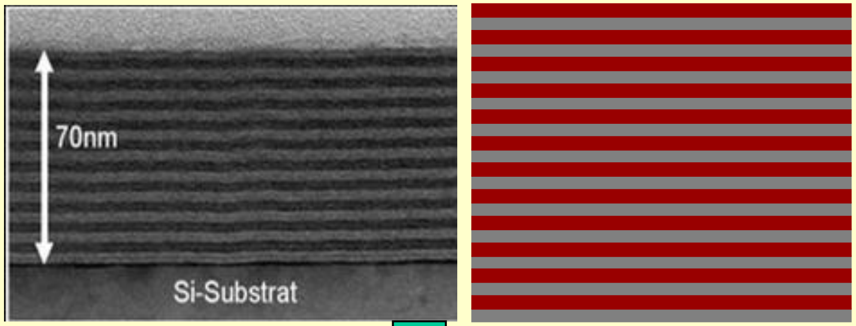
Incremento de 0,8 a 1,4

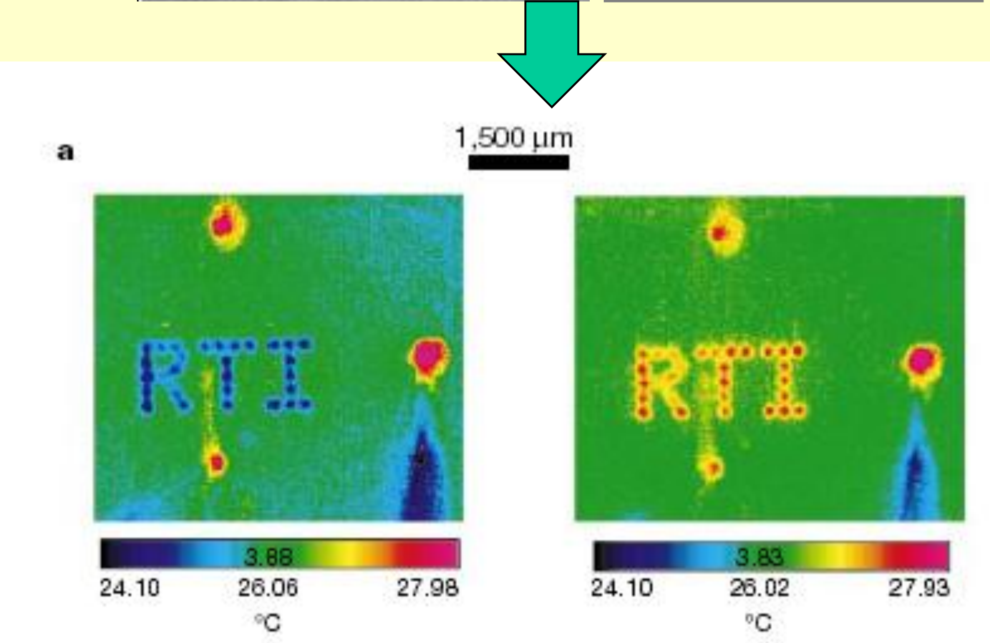


Superredes

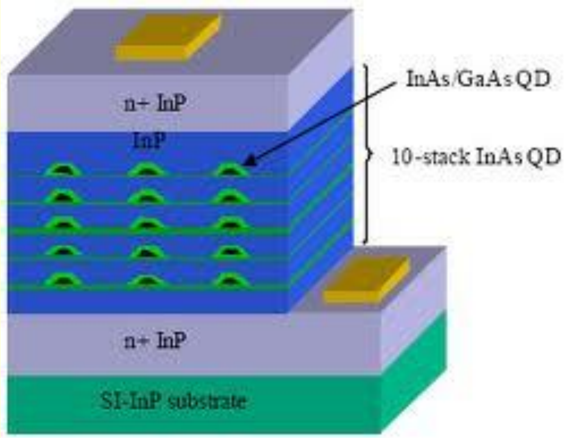


SLs PbSe/PbTe



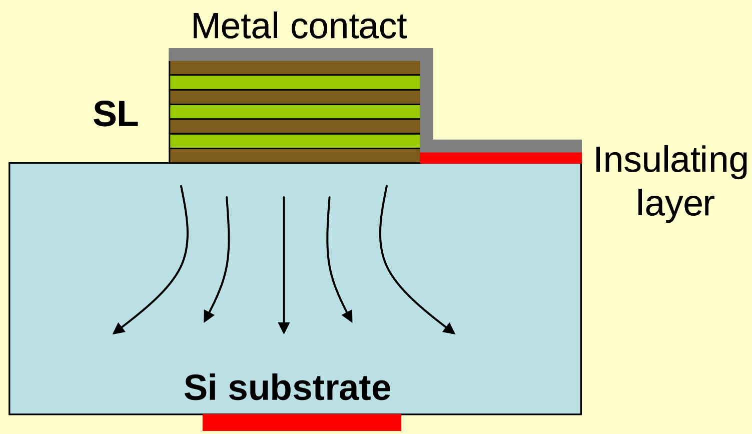


Venkatusabramanian, Nature 2001



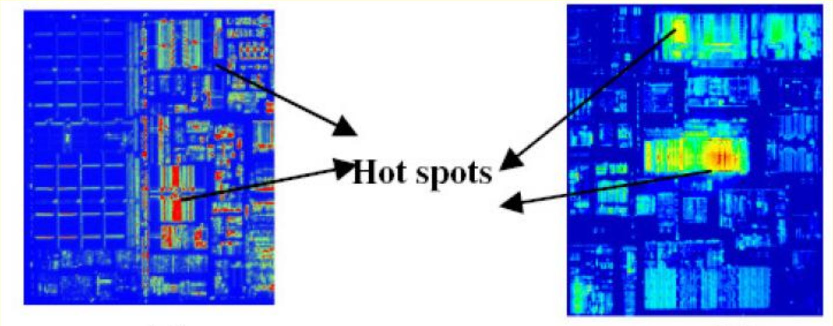
Aplicaciones --- Nanorefrigerador

Integración de SiGe en circuitos integrados base Silicio

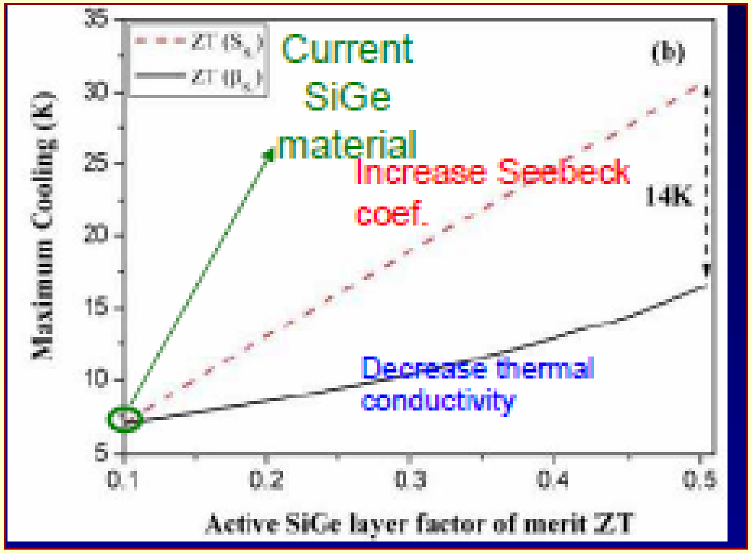


↑↑↑↑↑↑ ~700 W/cm^2

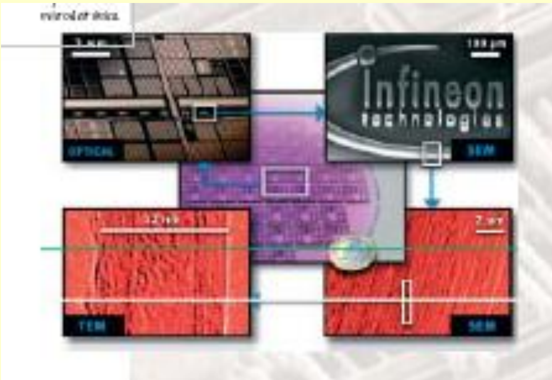
Zona caliente

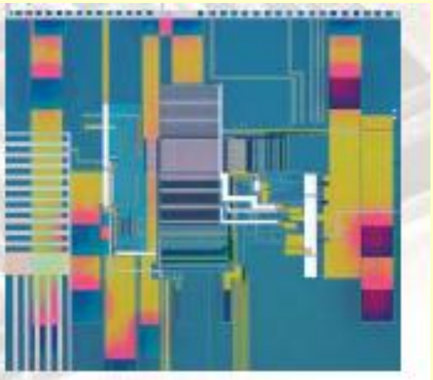


microrefrigerador con ZT~0.5
enfriamiento 1000 W/cm^2 en 15ºC



Ezzhari et al. interPACK07

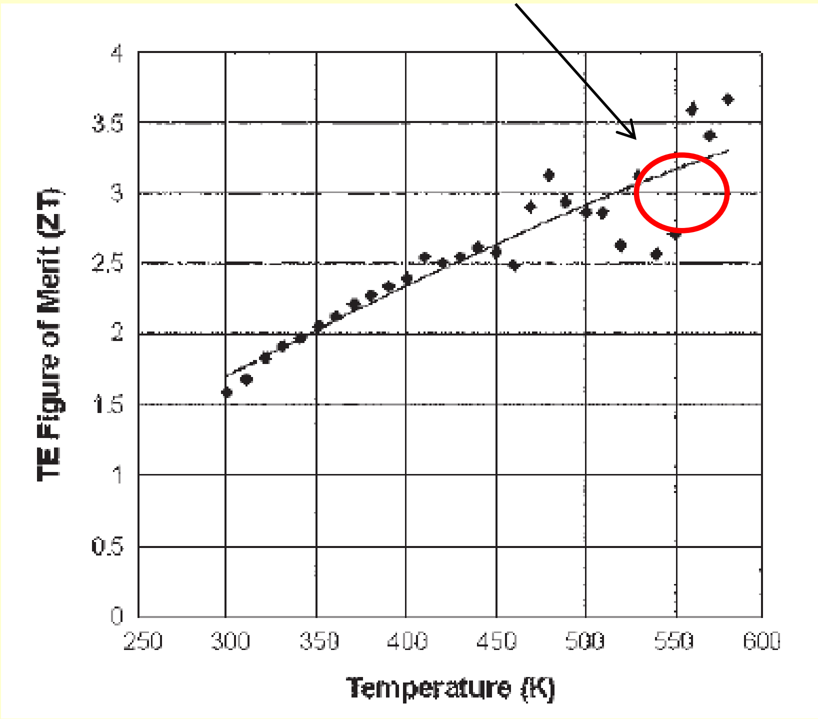


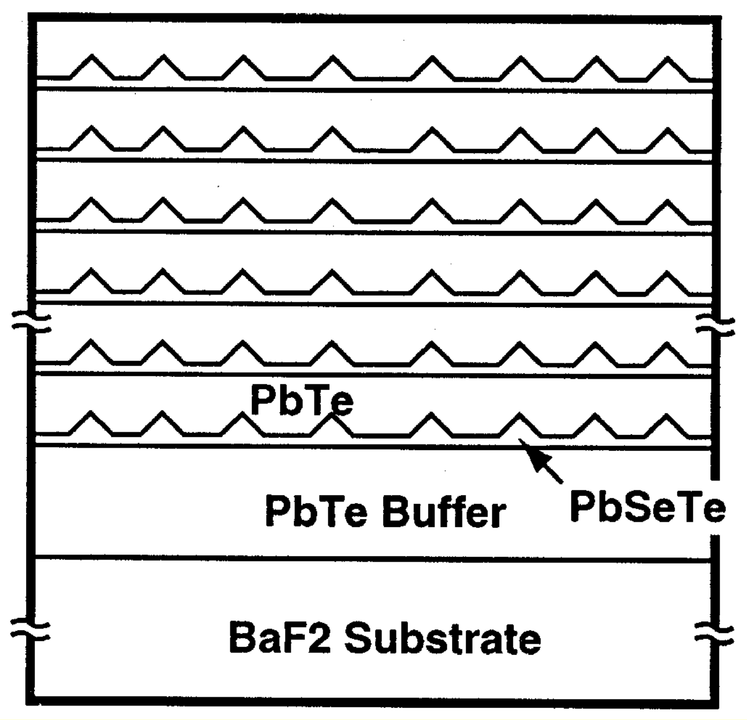


Record mundial termoeléctrico

Bi-doped n-type PbSeTe/PbTe quantum dot superlattice (QDSL)

ZT=3 a 550 K

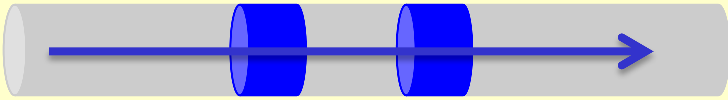


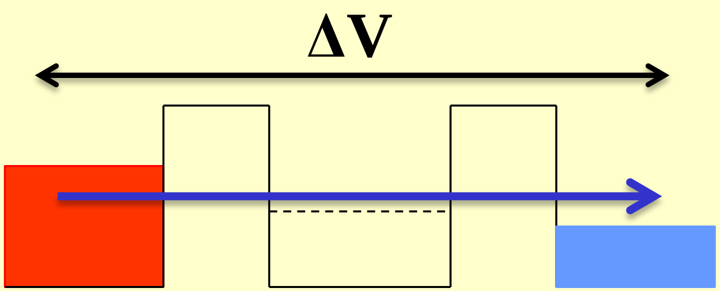


Estructuras Túnel Resonantes -- Futuro prometedor

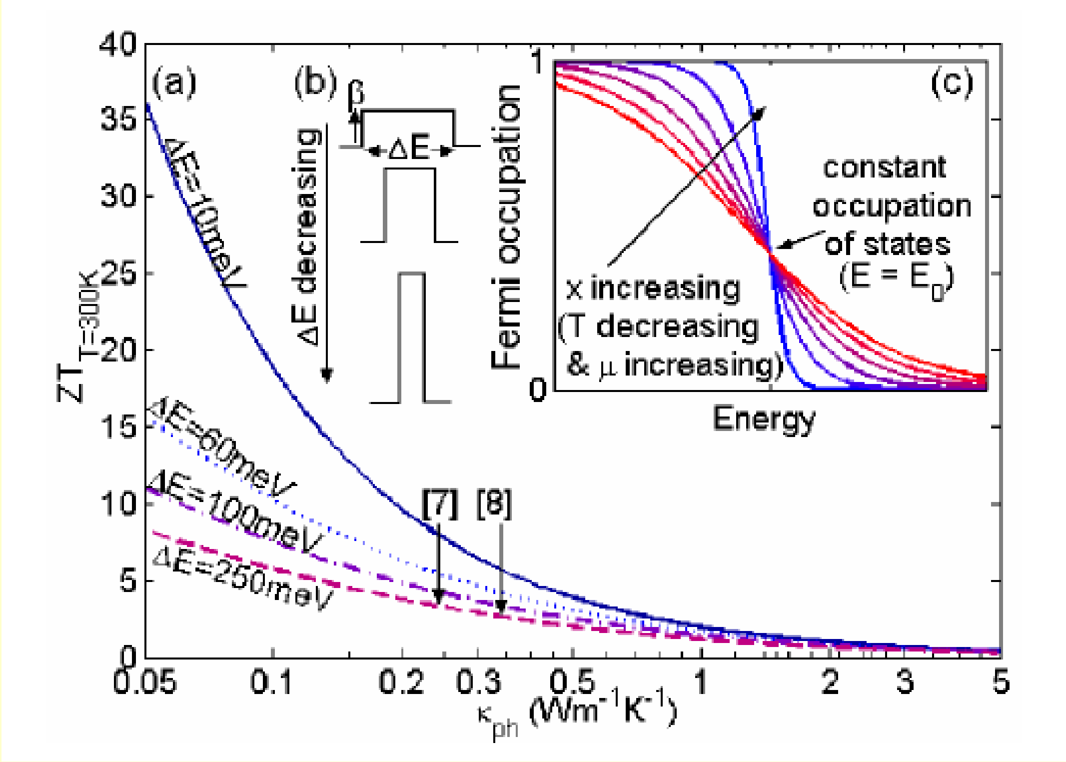
Bloquean la conducción de electrones excepto para la energía del nivel resonante

Si se pudiera eliminar la contribución de la red a la conductividad térmica, la figura de mérito podría incrementarse sustancialmente





$$ZT = ZT^{(el)} \frac{1}{1+\kappa^{(ph)}/\kappa^{(el)}}$$



Perspectivas

- Los límites inferiores de conductividad térmica están cerca, aunque quizás estructuras más complejas puedan dar lugar a k más bajas.
- Los efectos de dimensionalidad juegan un papel muy relevante en las propiedades físicas de los materiales, en particular pueden aumentar de forma significativa el coeficiente Seebeck.
- El filtrado electrónico promete ser una vía interesante de investigación futura.
- El dispositivo termoeléctrico también debe optimizarse para conseguir un uso amplio de la termoelectricidad.
- ZT=3-4 abre las puertas a un uso generalizado de dispositivos termoeléctricos para la conversión de energía.

GRACIAS