

# Propiedades Ópticas de Semiconductores.

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**Table 11.1** Survey of logical steps in the derivation of the classical expressions for the optical constants (left column), and the semiclassical treatment (right column)

Classical treatment	Semiclassical treatment	
<i>Basic equations</i>		
Newton: $\mathbf{F} = m\mathbf{a}$	Schrödinger: $i\hbar \frac{\partial \Psi}{\partial t} = \mathbf{H}\Psi$	Von-Neumann: $i\hbar \frac{\partial}{\partial t} \rho = [\mathbf{H}, \rho]$
<i>Model assumptions</i>		
$\mathbf{F} = \mathbf{F}_{restore} + \mathbf{F}_{damping} + \mathbf{F}_{Coulomb}$	$\mathbf{H} = \mathbf{H}_{0U} + \mathbf{H}_{0S} + \mathbf{H}_{SU} + \mathbf{V}$	
<i>“Unperturbed” system</i>		
$F_{restore} = -m\omega_0^2 x$	$\mathbf{H}_0 = \mathbf{H}_{0U} + \mathbf{H}_{0S}$	
<i>Damping (interaction with the environment)</i>		
$F_{damping} = -2\gamma m \dot{x}$	$[\mathbf{H}_{SU}, \rho]_{nm} \equiv -\frac{i\hbar \rho_{nm}}{T_{2(nm)}}$	
<i>Interaction with the (local) electric field of the perturbing wave</i>		
$F_{Coulomb} = qE \rightarrow qE_{micr}$	$\mathbf{V} = -p\mathbf{E} \rightarrow -p\mathbf{E}_{micr}$	
Newton’s equation of motion: $qE = m\ddot{x} + 2\gamma m \dot{x} + m\omega_0^2 x$	Von-Neumann equation in the interaction picture: $i\hbar \frac{\partial}{\partial t} \rho_{nm} = [\mathbf{V}, \rho]_{nm} + [\mathbf{H}_{SU}, \rho]_{nm}$	
<i>Microscopic dipole moment</i>		
$p = qx$	$p \rightarrow \langle p \rangle = Tr(p\rho)$	
Microscopic linear material equation: $p = \epsilon_0 \beta E_{micr}$		
<i>Microscopic polarizability</i>		
Single oscillator model: $\beta = \beta(\omega) = \frac{q^2}{\epsilon_0 m \omega_0^2 - \omega^2 - 2i\omega\gamma}$	Two-level-system: $\beta = \beta(\omega) = \frac{ p_{12} ^2}{\epsilon_0 \hbar} \cdot 2\omega_{21} \frac{(\rho_{11}^{(0)} - \rho_{22}^{(0)})}{\omega_{21}^2 + \Gamma^2 - \omega^2 - 2i\omega\Gamma}$	
Generalization to multioscillator model: $\beta = \beta(\omega) = \frac{q^2}{\epsilon_0 m} \sum_{j=1}^M \frac{f_j}{\omega_{0j}^2 - \omega^2 - 2i\omega\Gamma_j}$	Generalization to systems with many energy levels: $\beta = \beta(\omega) = \sum_l \sum_{n>l} \frac{ p_{nl} ^2}{\epsilon_0 \hbar} \cdot 2\omega_{nl} \cdot \frac{(\rho_{ll}^{(0)} - \rho_{nn}^{(0)})}{\omega_{nl}^2 + \Gamma_{nl}^2 - \omega^2 - 2i\omega\Gamma_{nl}}$	
<i>Macroscopic dielectric function and optical constants</i>		
$\frac{\epsilon(\omega)-1}{\epsilon(\omega)+2} = \frac{N\beta(\omega)}{3} \Leftrightarrow \hat{n}(\omega) = n(\omega) + iK(\omega) \equiv \sqrt{\epsilon(\omega)}$		

# Propiedades Ópticas de Semiconductores

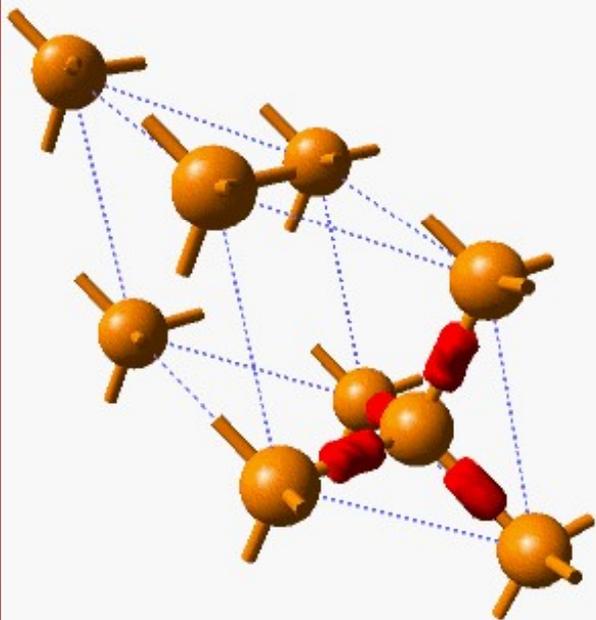
- **Estructura Electrónica**
- **Absorción Óptica en Semiconductores**
- **Influencia de Defectos**
- **Excitones**
- **Efectos Nanométricos**

# Propiedades Ópticas de Semiconductores

- **Estructura Electrónica**
- **Absorción Óptica en Semiconductores**
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- **Efectos Nanométricos**

# Materiales Cristalinos

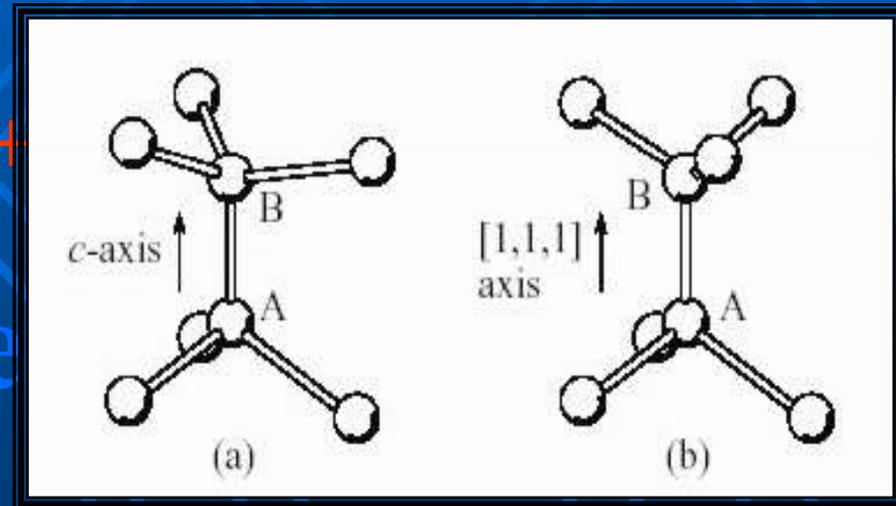
Diamante



Wurtzite  
(hexagonal)

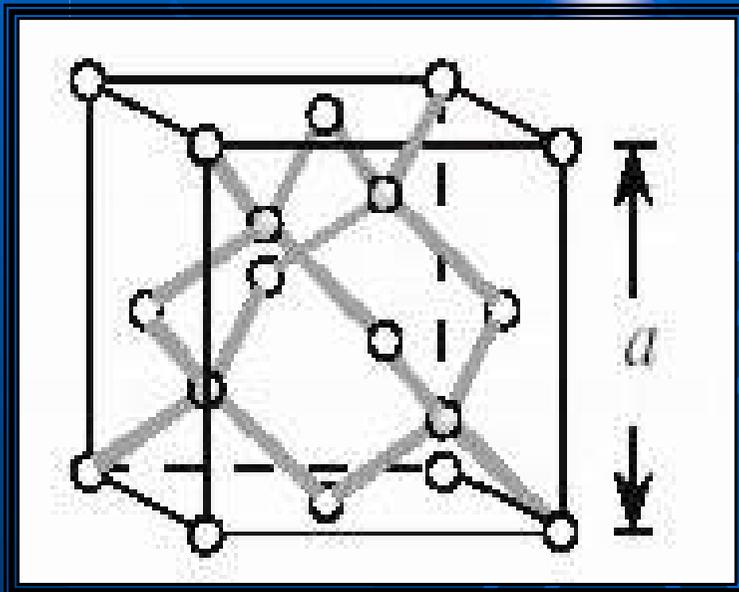
Zincblende  
(cúbica)

$e^-$   
 $4e^-$   
 $e^-$



# Materiales Cristalinos

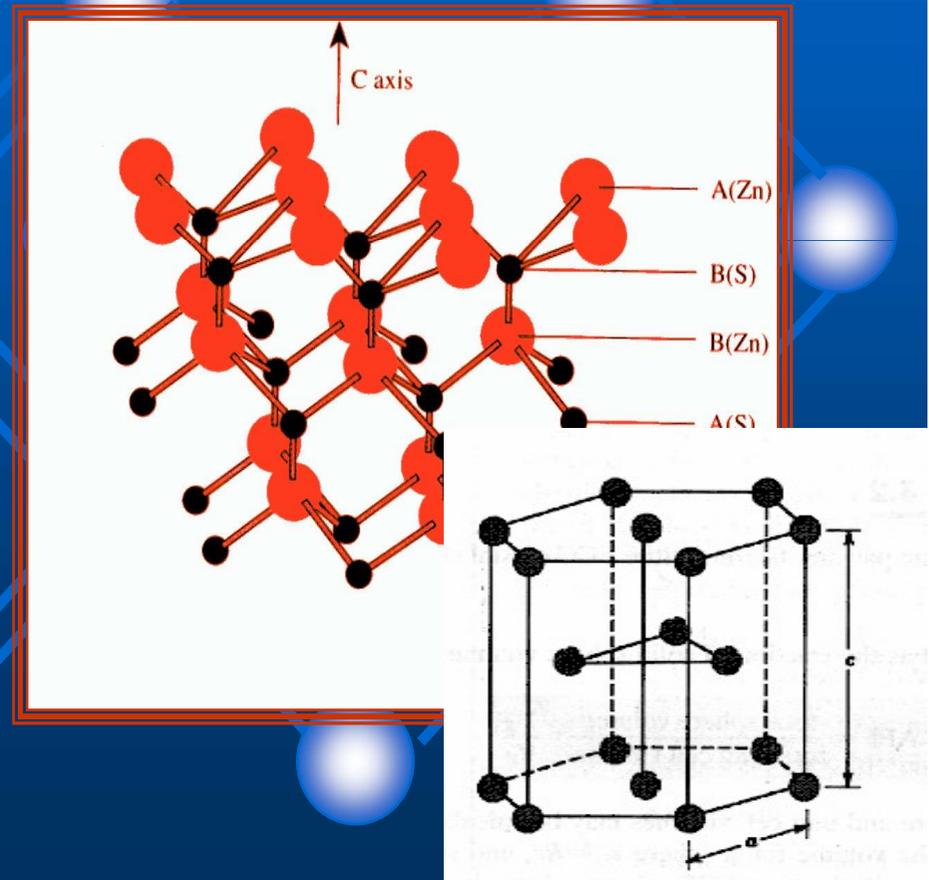
Diamante



$e^-$   
 $4e^+$

$e^-$

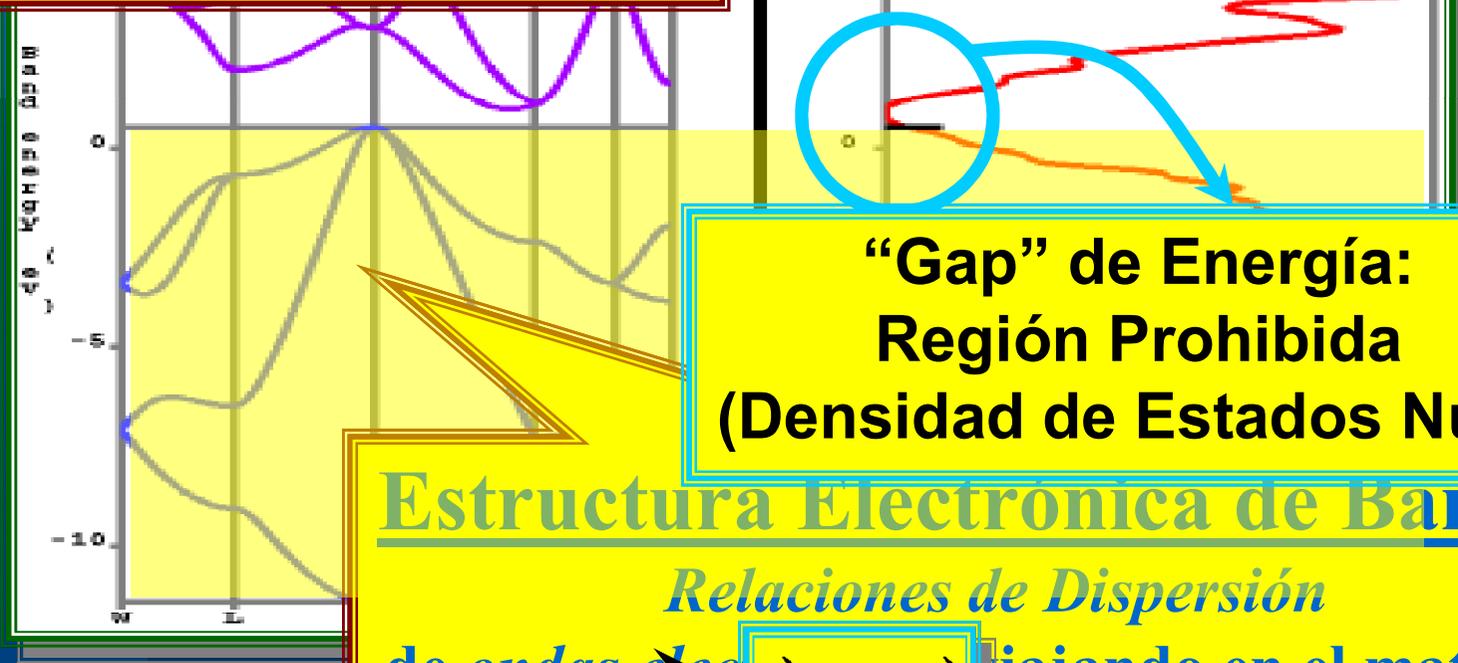
Wurtzite  
(hexagonal)



# Estructura Electrónica (Caso: Silicio)

## Densidad de Estados

*Número de Estados Disponibles  
por Intervalo de Energía  
(Influye directamente  
Propiedades Ópticas)*



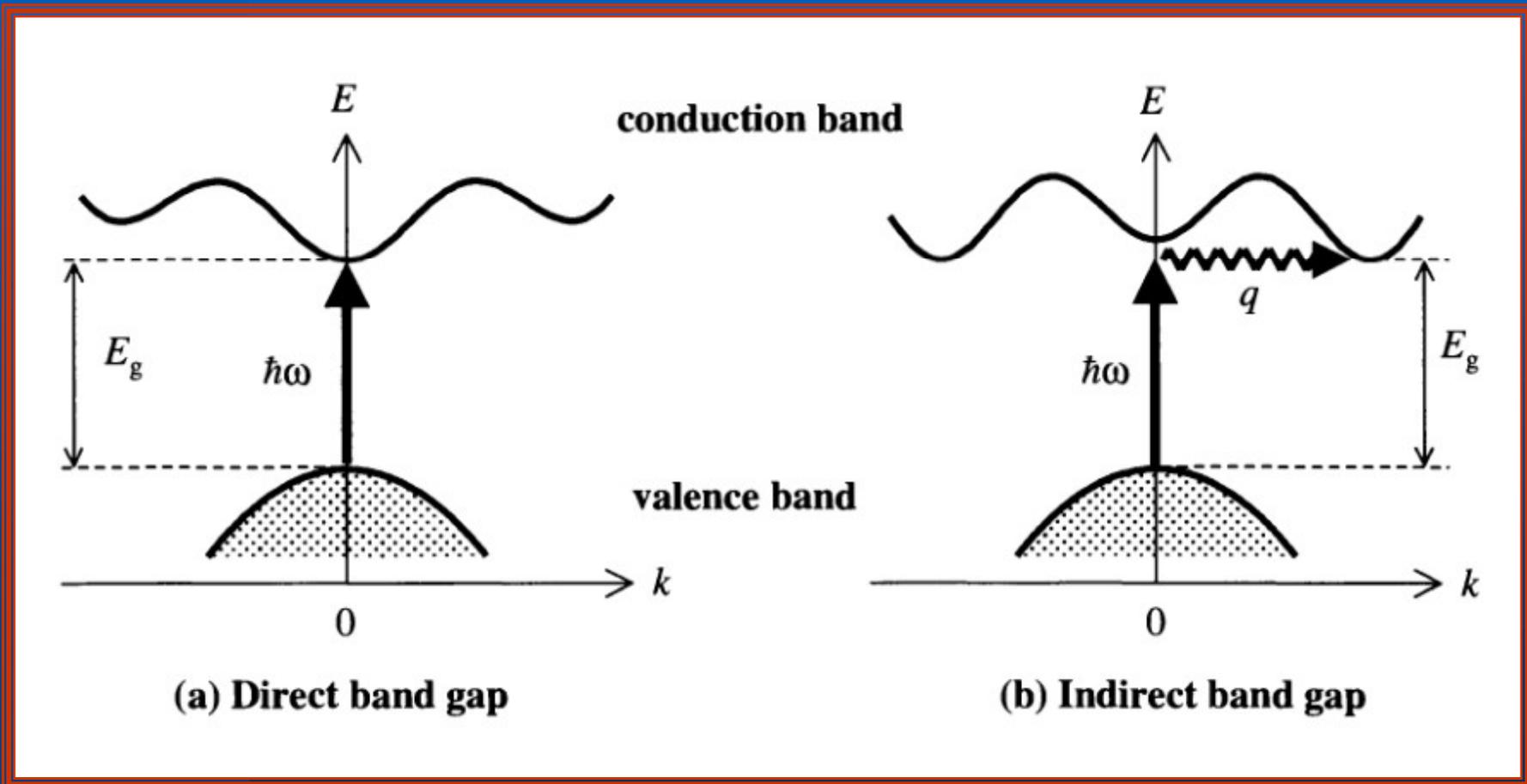
**“Gap” de Energía:  
Región Prohibida  
(Densidad de Estados Nula)**

## Estructura Electrónica de Bandas

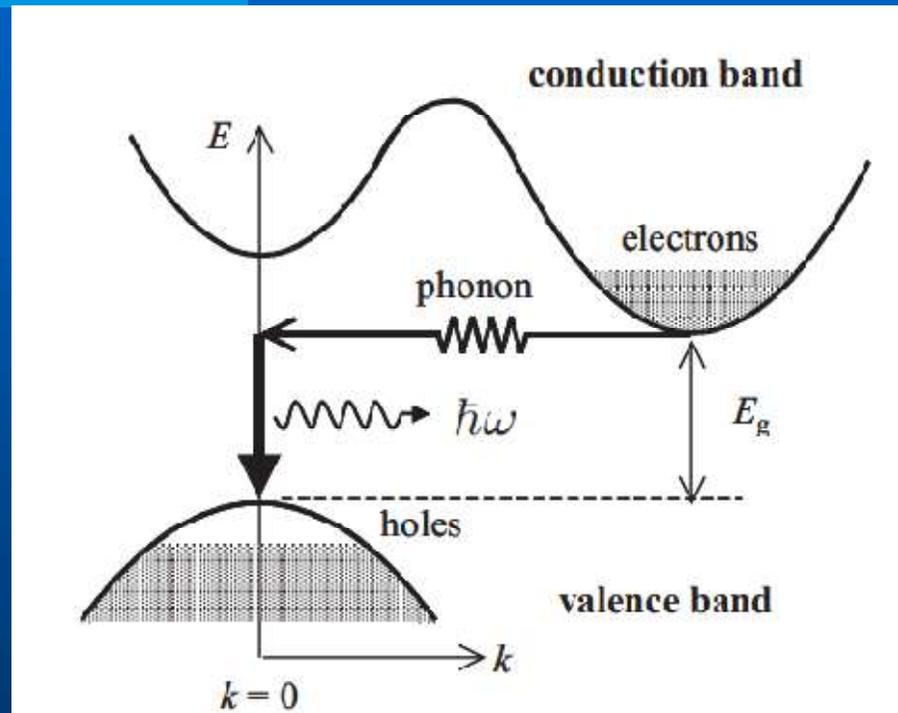
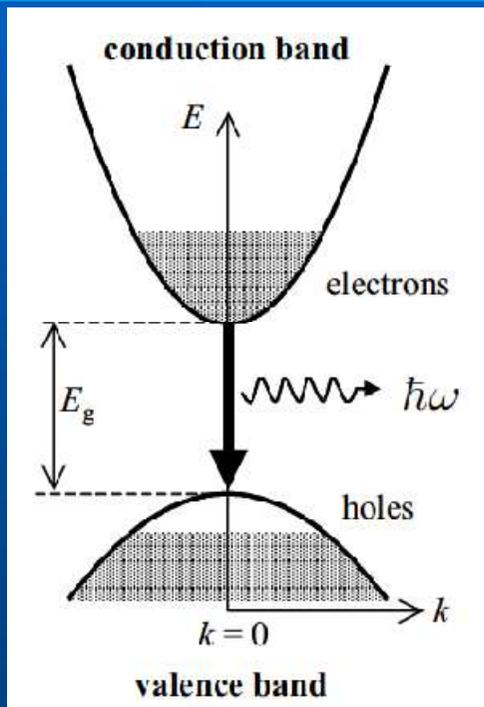
*Relaciones de Dispersión  
de ondas viajando en el material.*

$$\vec{p} = \hbar \vec{k}$$

# Borde de Bandas de Energía: Semiconductores Directo e Indirecto



# Borde de Bandas de Energía: Semiconductores Directo e Indirecto



Semiconductor *Directo*  $\Rightarrow$  Buen Emisor de Luz.

Semiconductor *Indirecto*  $\Rightarrow$  Mal Emisor de Luz.

Silicio y Germanio son Semiconductores Indirectos

# Tabla Periódica de los Elementos

Nome degli elementi

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra																
		Terre rare															
Lantanidi		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb		
Attinidi		Ac	Th	Pa	U	Np	Pu										

Gruppo I Alcalini  
 Gruppo II Alcalino terrosi  
 Gruppo III  
 Gruppo IV  
 Gruppo V  
 Gruppo VI  
 Gruppo VII  
 Gruppo VIII  
 Gruppi di transizione

Aleaciones  
Semicond.

# Semiconductores más comunes

II III IV V VI

- Si - Ge: Grupos IV  
Estructura Diamante y Gap Indirecto
- Aleaciones Binarias:  
Generalmente (NO siempre), estructura Zincblende o Wurtzite y Gap Directo
- Grupos III-V (GaAs):  
(Al, Ga, In) (N P As Sb)
- Grupos II-VI:  
(Zn, Cd, Hg) (O, S, Se, Te)
- Grupos II-IV-V<sub>2</sub>, I-III-VI<sub>2</sub>
- Grupos IV-VI (PbTe, PbS):
- Óxidos:  
ZnO, CdO, CuO, Cu<sub>2</sub>O, Ti<sub>2</sub>O

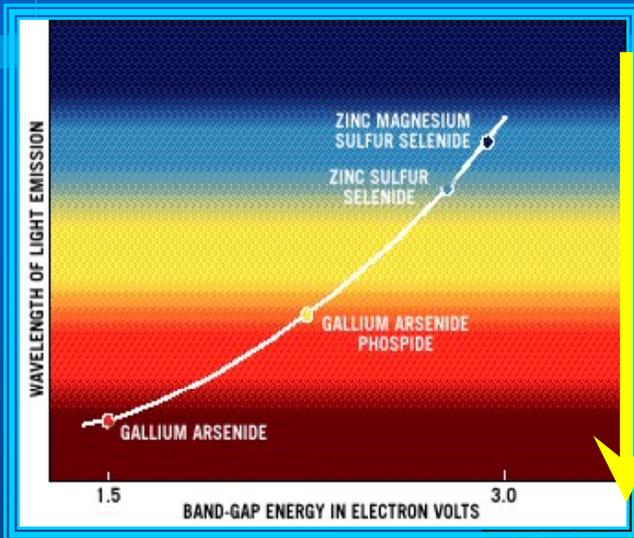
			19.211 5 <b>B</b> [He] 2s <sup>2</sup> 2p <sup>1</sup> mp: 2000 °C d: 2.46 g/cc Boron	12.011 6 <b>C</b> [He] 2s <sup>2</sup> 2p <sup>2</sup> mp: 3550 °C d: 3.51 g/cc Carbon	14.00674 7 <b>N</b> [He] 2s <sup>2</sup> 2p <sup>3</sup> bp: -195.8 °C d: 1.17 g/l Nitrogen	15.9994 8 <b>O</b> [He] 2s <sup>2</sup> 2p <sup>4</sup> bp: -183.0 °C d: 1.33 g/l Oxygen
			26.981538 13 <b>Al</b> [Ne] 3s <sup>2</sup> 3p <sup>1</sup> mp: 933.4 °C d: 2.70 g/cm <sup>3</sup> Aluminium	28.0855 14 <b>Si</b> [Ne] 3s <sup>2</sup> 3p <sup>2</sup> mp: 1410 °C d: 2.33 g/cm <sup>3</sup> Silicon	30.97376 15 <b>P</b> [Ne] 3s <sup>2</sup> 3p <sup>3</sup> mp: 44.1 °C d: 2.34 g/cm <sup>3</sup> Phosphorus	32.06 16 <b>S</b> [Ne] 3s <sup>2</sup> 3p <sup>4</sup> mp: 115.2 °C d: 2.08 g/cm <sup>3</sup> Sulfur
11 IB	12 IIB					
63.546 29 <b>Cu</b> [Ar] 3d <sup>10</sup> 4s <sup>1</sup> mp: 1083 °C d: 8.96 g/cm <sup>3</sup> Copper	65.38 30 <b>Zn</b> [Ar] 3d <sup>10</sup> 4s <sup>2</sup> mp: 912 °C d: 7.14 g/cm <sup>3</sup> Zinc	69.723 31 <b>Ga</b> [Ar] 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>1</sup> mp: 24.0 °C d: 5.91 g/cm <sup>3</sup> Gallium	72.64 32 <b>Ge</b> [Ar] 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>2</sup> mp: 937 °C d: 5.32 g/cm <sup>3</sup> Germanium	74.9216 33 <b>As</b> [Ar] 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>3</sup> mp: 611 °C d: 5.72 g/cm <sup>3</sup> Arsenic	78.96 34 <b>Se</b> [Ar] 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>4</sup> mp: 221 °C d: 4.48 g/cm <sup>3</sup> Selenium	
107.8682 47 <b>Ag</b> [Kr] 4d <sup>10</sup> 5s <sup>1</sup> mp: 962 °C d: 10.49 g/cm <sup>3</sup> Silver	112.411 48 <b>Cd</b> [Kr] 4d <sup>10</sup> 5s <sup>2</sup> mp: 321 °C d: 8.65 g/cm <sup>3</sup> Cadmium	114.818 49 <b>In</b> [Kr] 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>1</sup> mp: 156.6 °C d: 7.31 g/cm <sup>3</sup> Indium	118.710 50 <b>Sn</b> [Kr] 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>2</sup> mp: 232 °C d: 7.31 g/cm <sup>3</sup> Tin	121.75 51 <b>Sb</b> [Kr] 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>3</sup> mp: 361 °C d: 6.09 g/cm <sup>3</sup> Antimony	127.46 52 <b>Te</b> [Kr] 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>4</sup> mp: 450 °C d: 6.25 g/cm <sup>3</sup> Tellurium	
196.9665 79 <b>Au</b> [Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>1</sup> mp: 1063 °C d: 19.32 g/cm <sup>3</sup> Gold	200.59 80 <b>Hg</b> [Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> mp: 388.3 °C d: 13.55 g/cm <sup>3</sup> Mercury	204.38 81 <b>Tl</b> [Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>1</sup> mp: 304 °C d: 11.85 g/cm <sup>3</sup> Thallium	207.2 82 <b>Pb</b> [Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>2</sup> mp: 327 °C d: 11.34 g/cm <sup>3</sup> Lead	208.9804 83 <b>Bi</b> [Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>3</sup> mp: 271 °C d: 9.78 g/cm <sup>3</sup> Bismuth	208.9804 84 <b>Po</b> [Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>4</sup> mp: 527 °C d: 9.19 g/cm <sup>3</sup> Polonium	

# Semiconductor $\Rightarrow$

## Energía del Gap

La Energía del Gap ( $E_g$ ) depende principalmente del material.

$$\lambda = hc/E_g$$

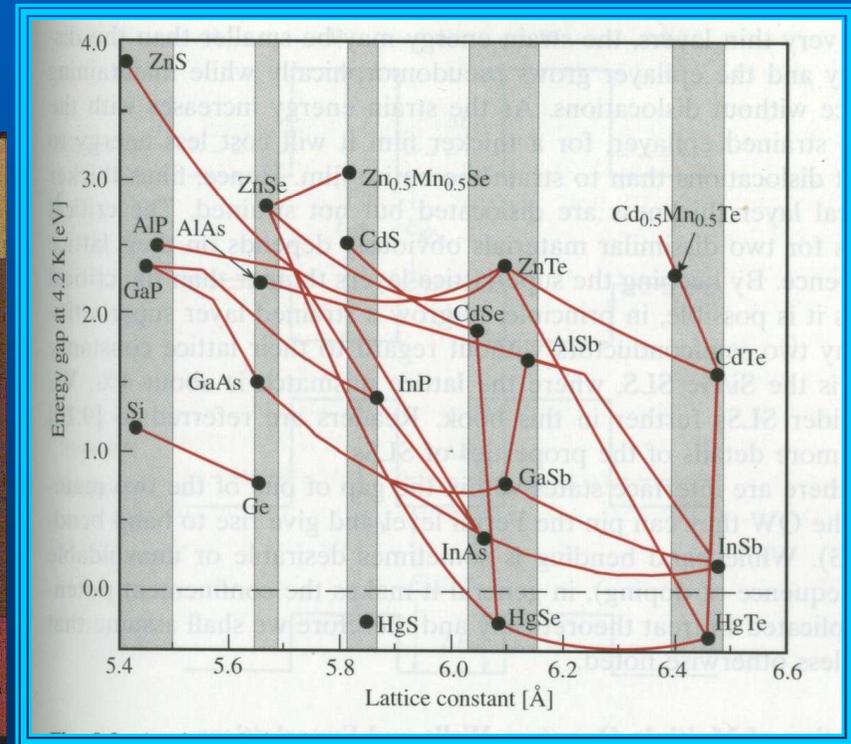


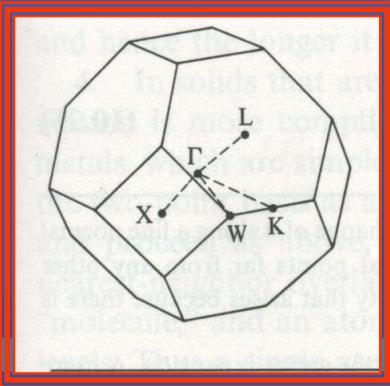
De  $E_g$  depende el **color** de la luz absorbida y emitida.

$$h\nu = hc/\lambda$$

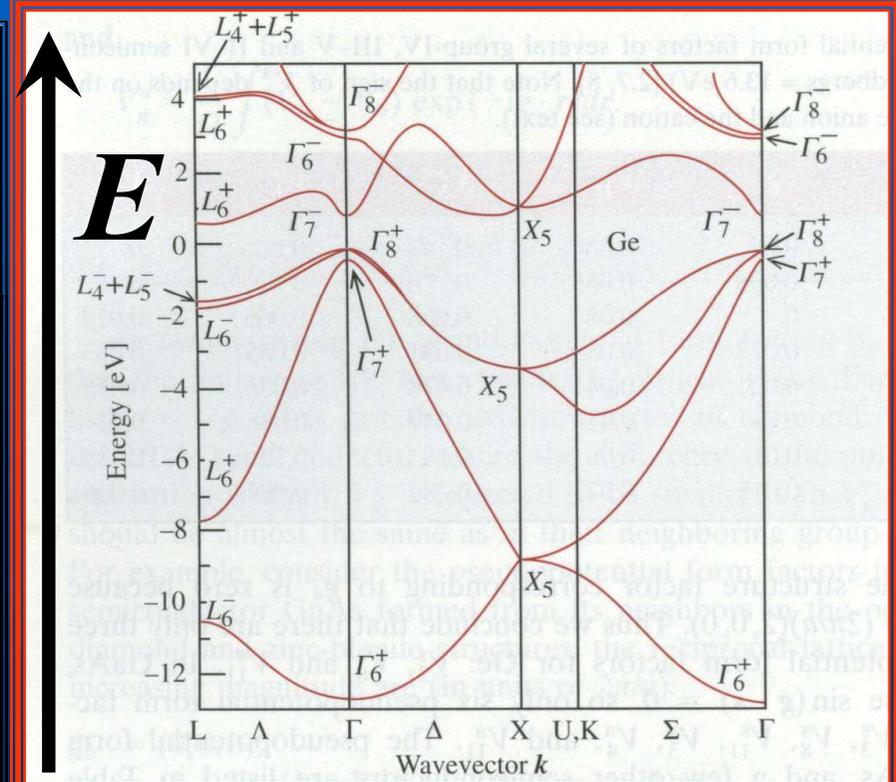
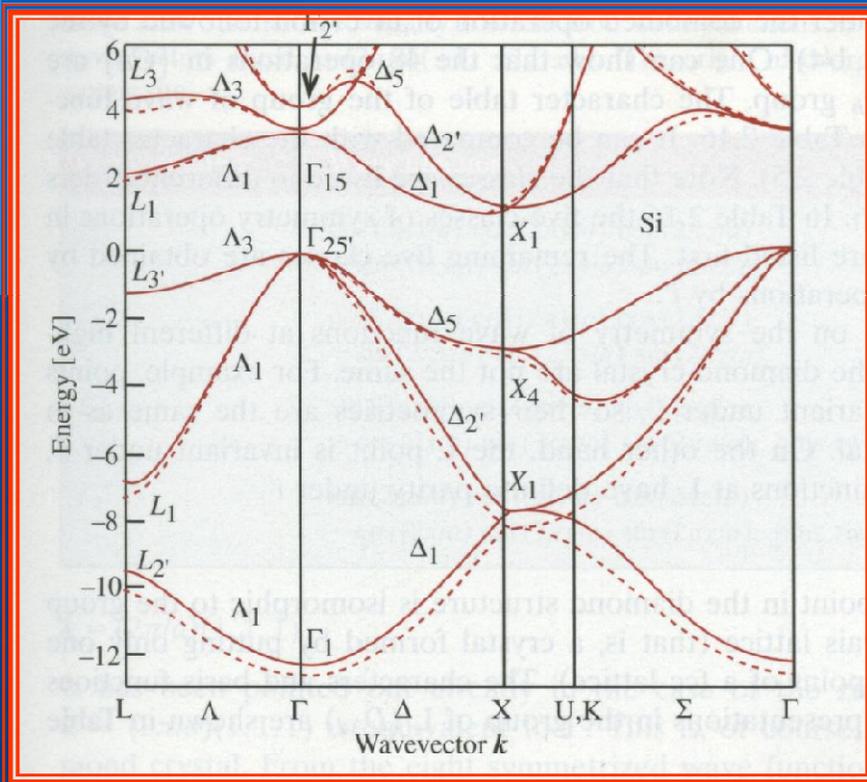
	B	C	N	O		
	107.252 g/mol mp: 2300 °C d: 2.48 g/cm³ Boron	12.011 g/mol mp: 3628 °C d: 3.51 g/cm³ Carbon	14.0064 g/mol mp: -199.8 °C d: 1.17 g/l Nitrogen	15.9994 g/mol mp: -183.0 °C d: 1.33 g/l Oxygen		
	Al	Si	P	S		
	26.9815 g/mol mp: 933 °C d: 2.70 g/cm³ Aluminum	28.0855 g/mol mp: 1410 °C d: 2.33 g/cm³ Silicon	30.973762 g/mol mp: 44.1 °C d: 2.34 g/cm³ Phosphorus	32.06 g/mol mp: 115.3 °C d: 2.07 g/cm³ Sulfur		
	Cu	Zn	Ga	Ge	As	Se
	63.546 g/mol mp: 1085 °C d: 8.96 g/cm³ Copper	65.38 g/mol mp: 419.5 °C d: 7.14 g/cm³ Zinc	69.723 g/mol mp: 24.8 °C d: 5.91 g/cm³ Gallium	72.630 g/mol mp: 121.1 °C d: 5.32 g/cm³ Germanium	74.9216 g/mol mp: 361 °C d: 5.78 g/cm³ Arsenic	78.96 g/mol mp: 221 °C d: 4.96 g/cm³ Selenium
	Ag	Cd	In	Sn	Sb	Te
	107.8682 g/mol mp: 961.78 °C d: 19.3 g/cm³ Silver	112.411 g/mol mp: 321 °C d: 8.65 g/cm³ Cadmium	114.818 g/mol mp: 15.7 °C d: 7.31 g/cm³ Indium	118.710 g/mol mp: 231.9 °C d: 7.26 g/cm³ Tin	121.757 g/mol mp: 477.3 °C d: 6.09 g/cm³ Antimony	127.6 g/mol mp: 422 °C d: 6.23 g/cm³ Tellurium
	Au	Hg	Tl	Pb	Bi	Po
	196.966569 g/mol mp: 1063 °C d: 19.3 g/cm³ Gold	200.59 g/mol mp: 239.8 °C d: 13.5 g/cm³ Mercury	204.3833 g/mol mp: 304.1 °C d: 11.85 g/cm³ Thallium	207.2 g/mol mp: 327.3 °C d: 11.34 g/cm³ Lead	208.9804 g/mol mp: 271.3 °C d: 9.78 g/cm³ Bismuth	209 g/mol mp: 234 °C d: 9.32 g/cm³ Polonium

II III IV V VI





# Silicio vs Germanio



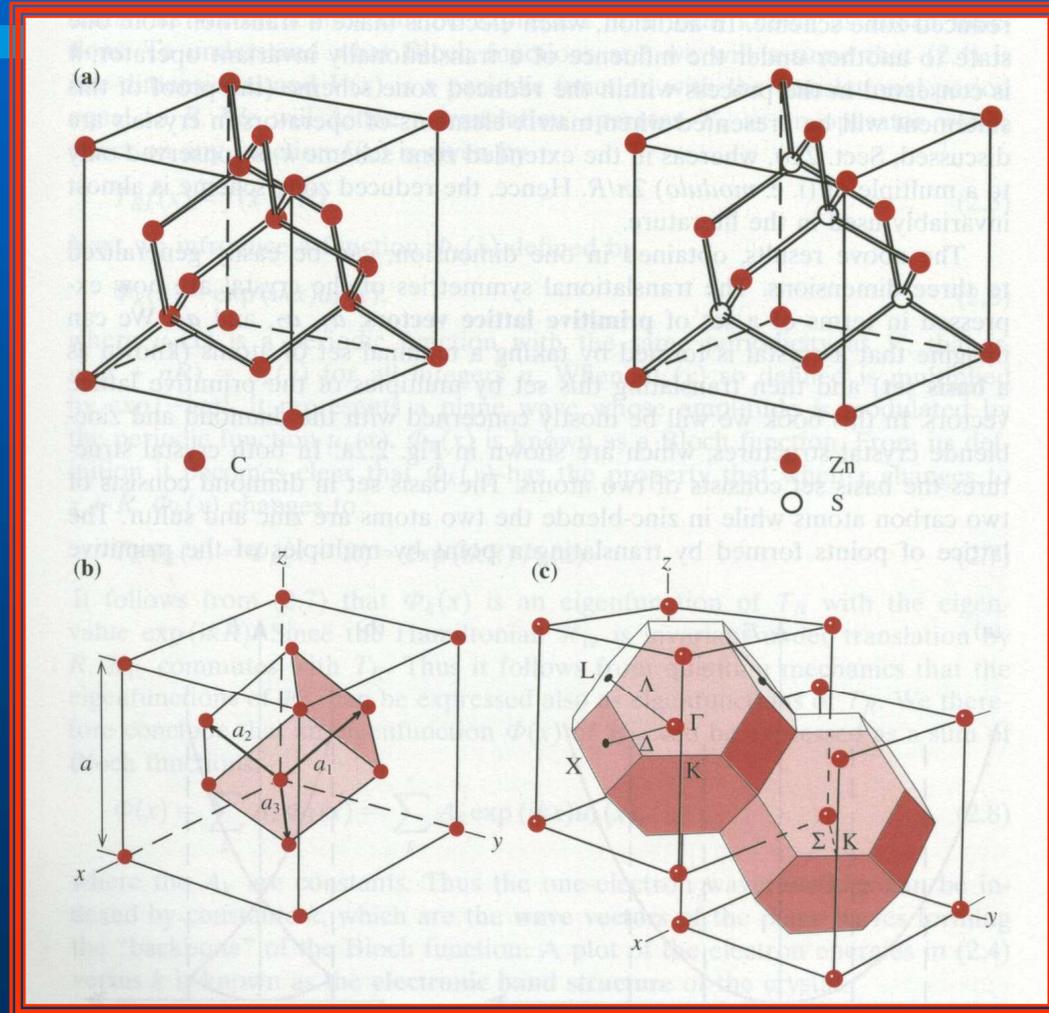
Silicio



$$\vec{p} = \hbar \vec{k}$$

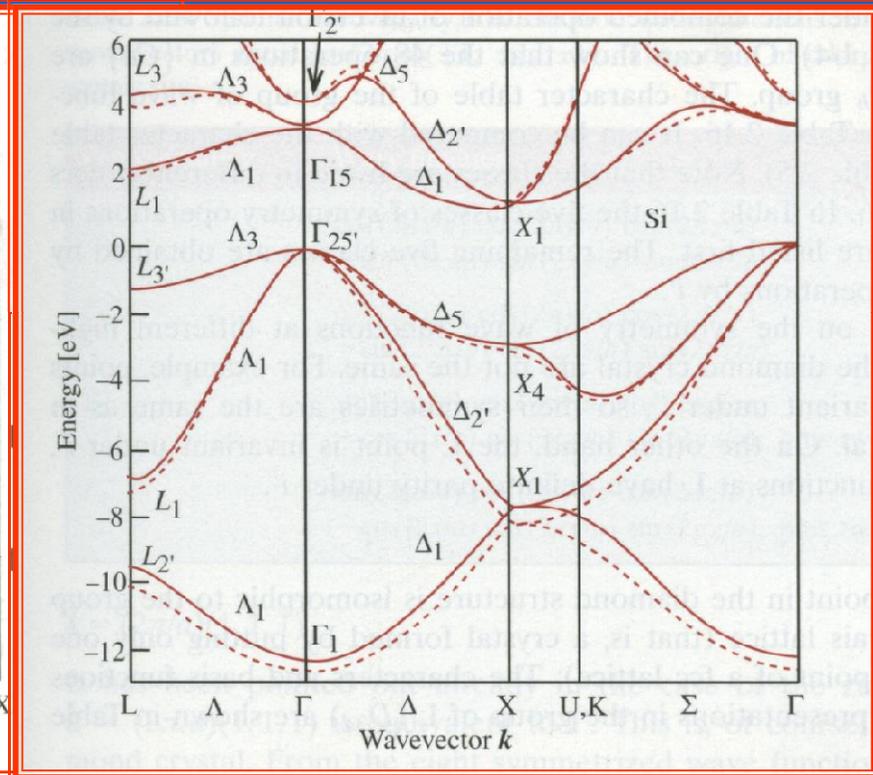
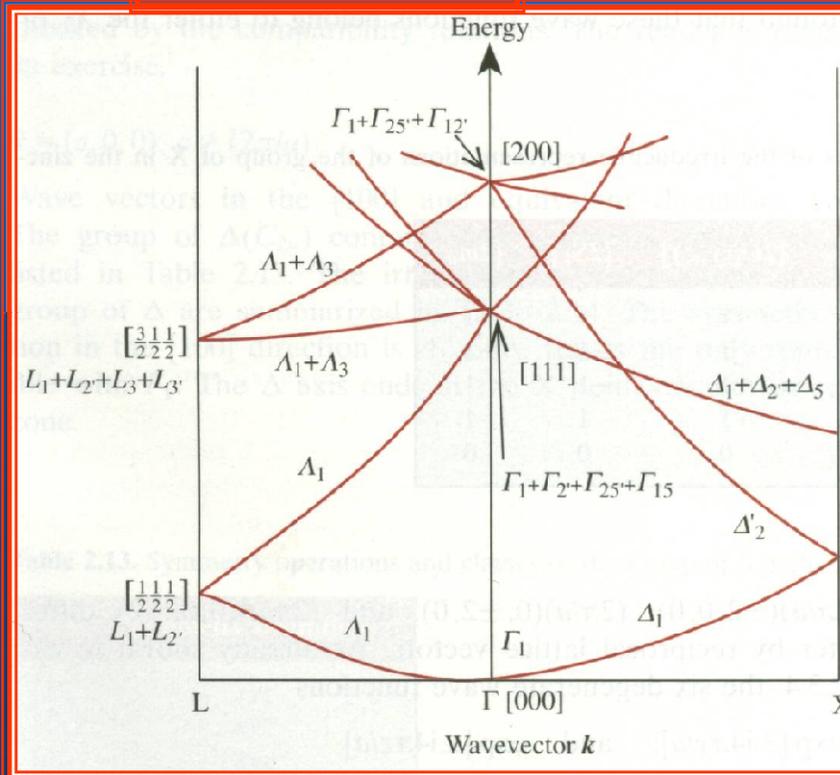
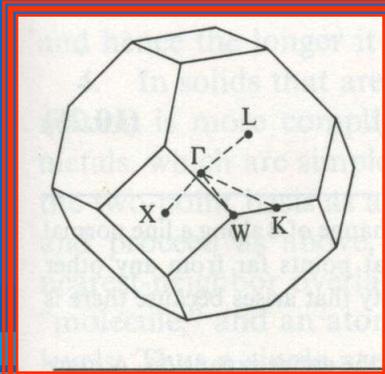
Germanio

# Diamante vs. ZincBlende



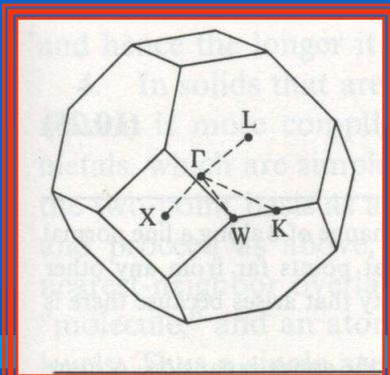


# Silicio (Diamante)

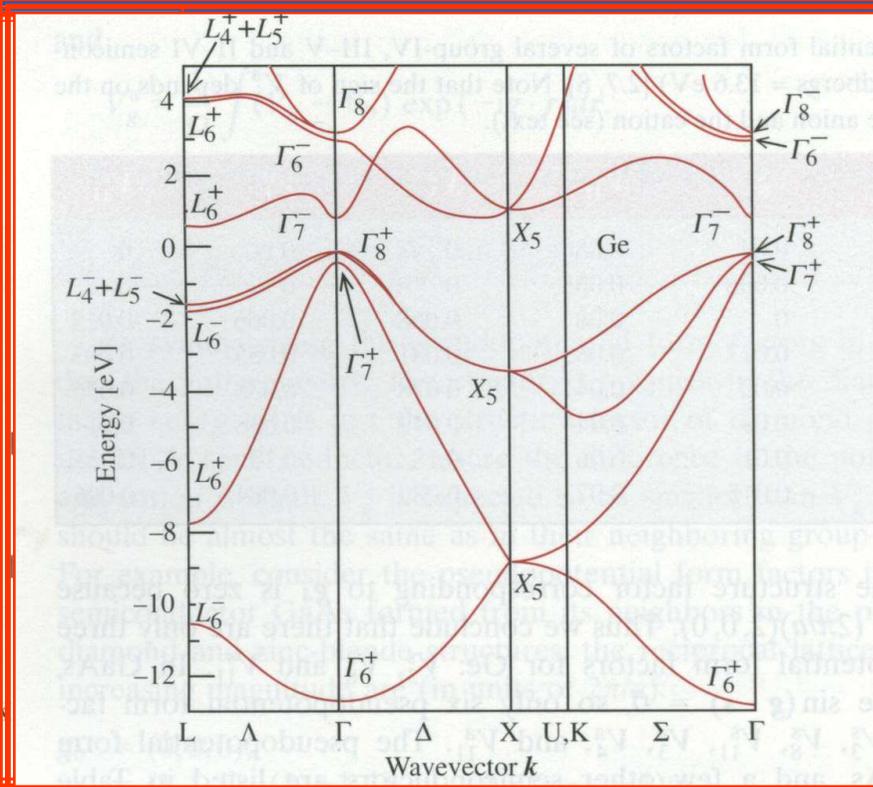
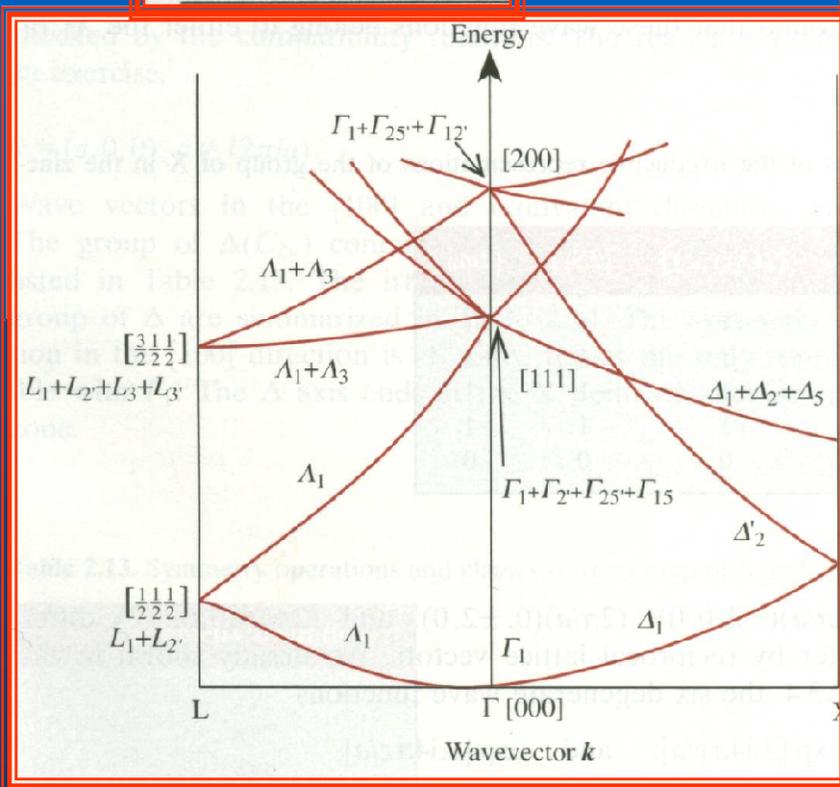


Estructura Electrónica del Electrón Libre.

Silicio



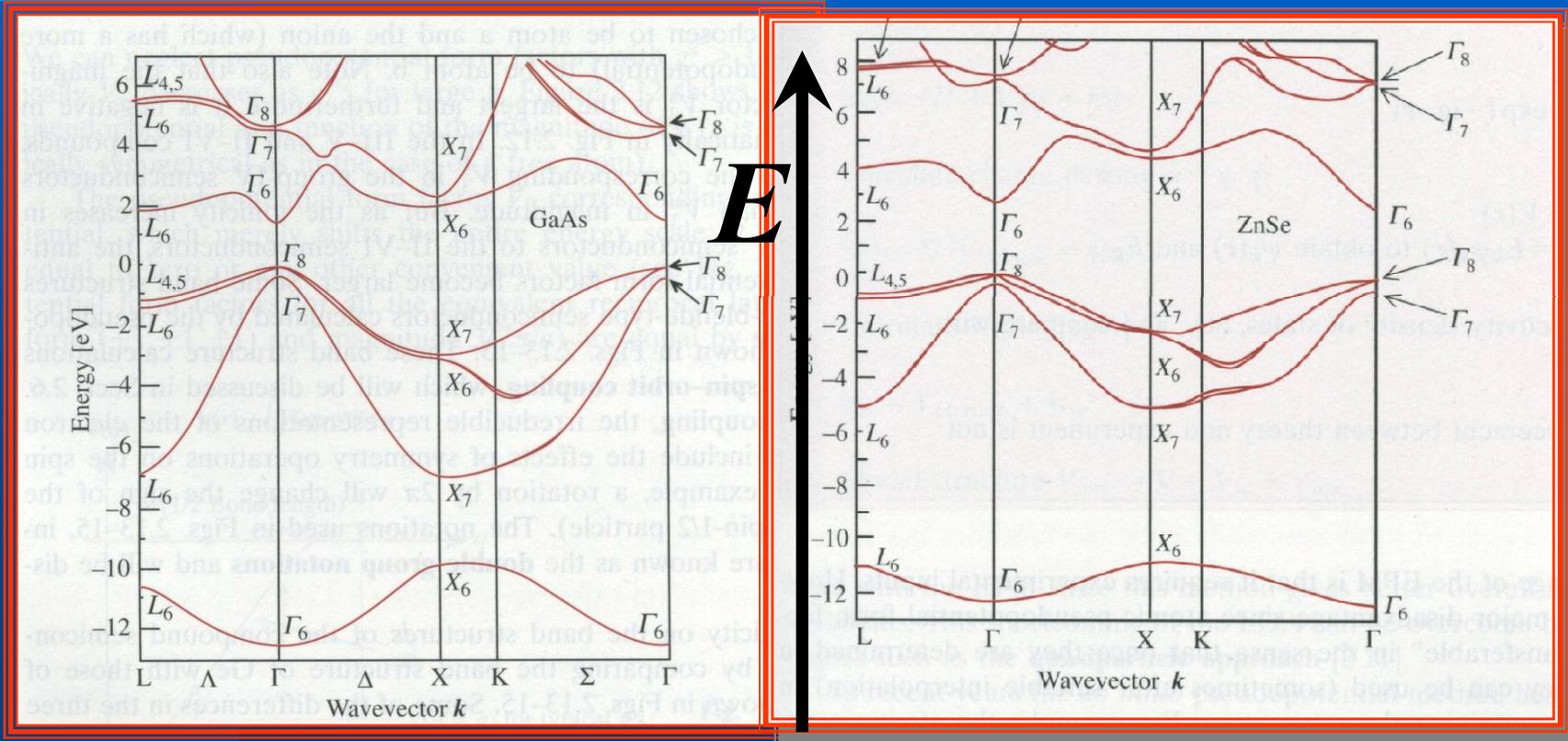
# Germanio (Diamante)



Estructura Electrónica del Electrón Libre.

Germanio

# GaAs vs ZnSe



GaAs



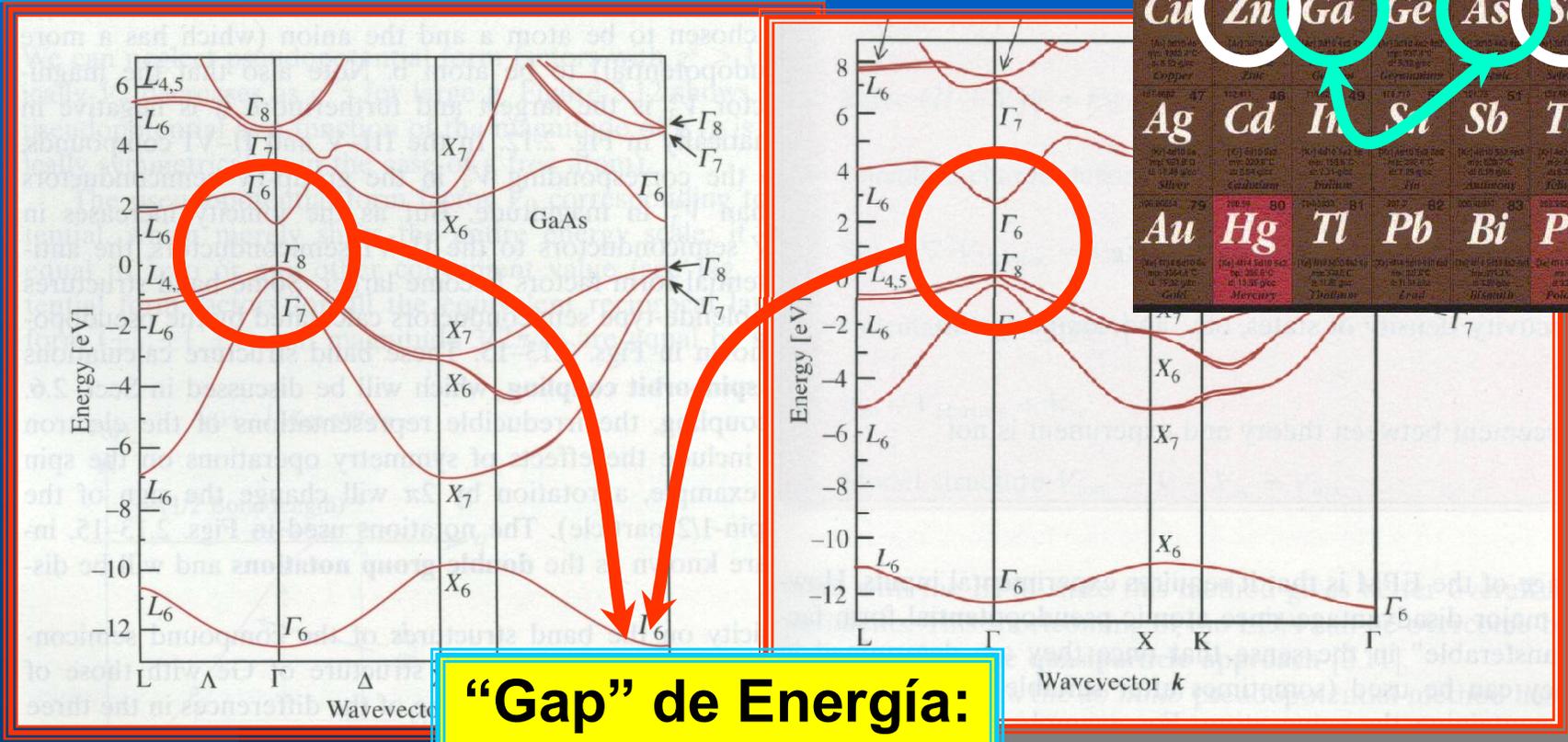
$$\vec{p} = \hbar \vec{k}$$

ZnSe

# GaAs vs ZnSe

II III IV V VI

	B	C	N	O	
	Al	Si	P	S	
	Zn	Ga	Ge	As	Se
	Cd	In	Sn	Sb	Te
	Hg	Tl	Pb	Bi	Po

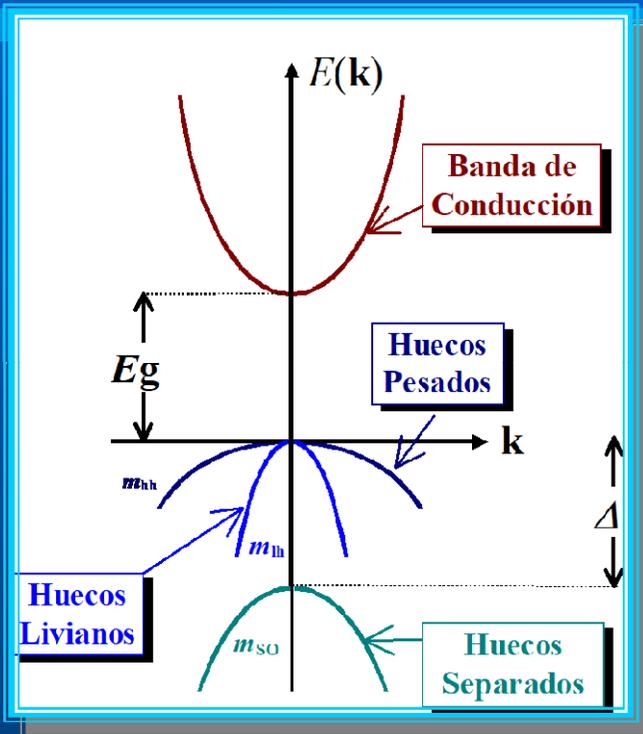


GaAs

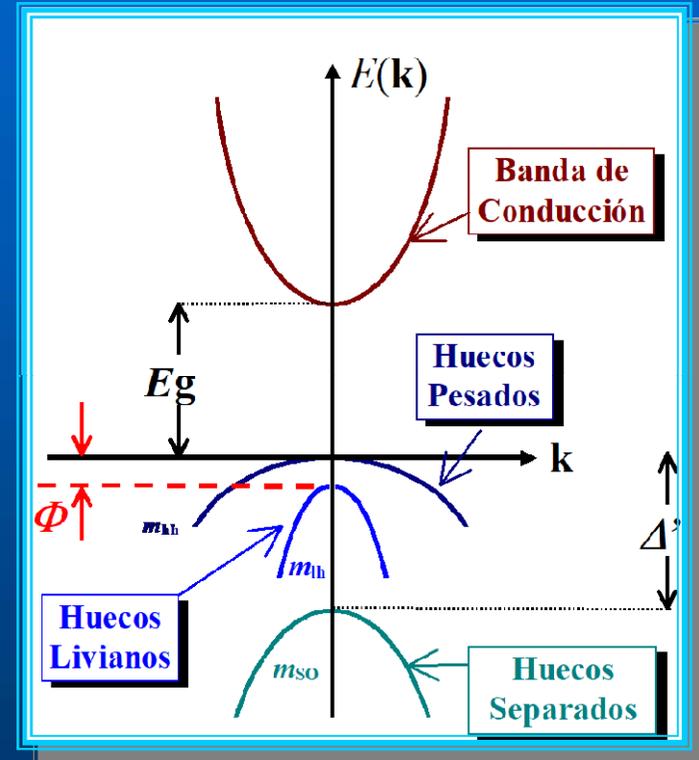
**“Gap” de Energía:  
Región Prohibida**

ZnSe

# Zincblende vs Wurtzite



$$E \approx \frac{p^2}{2m}$$



Zincblende  
(Cúbica)

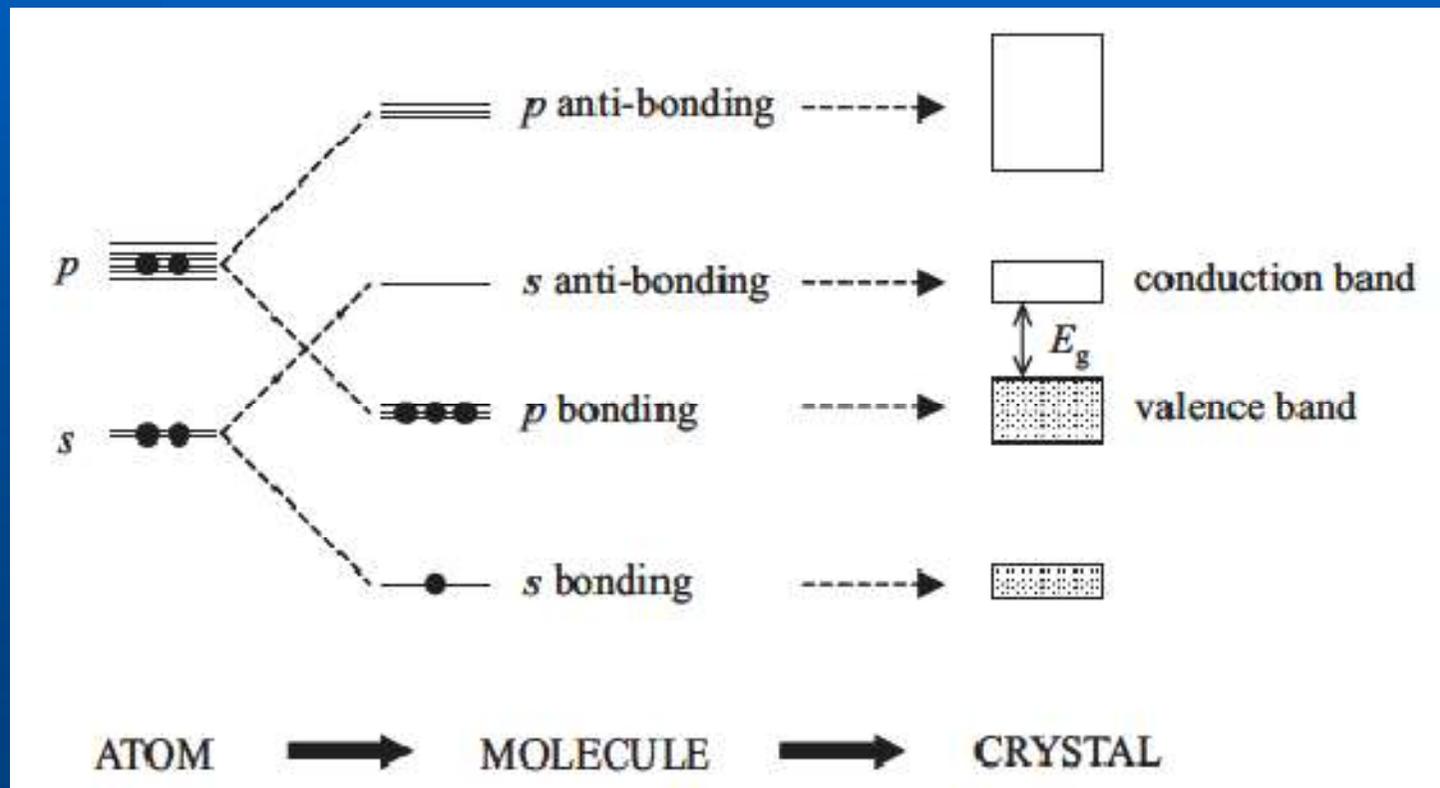
$\Delta$  - "Spin-Orbit"

Wurtzite

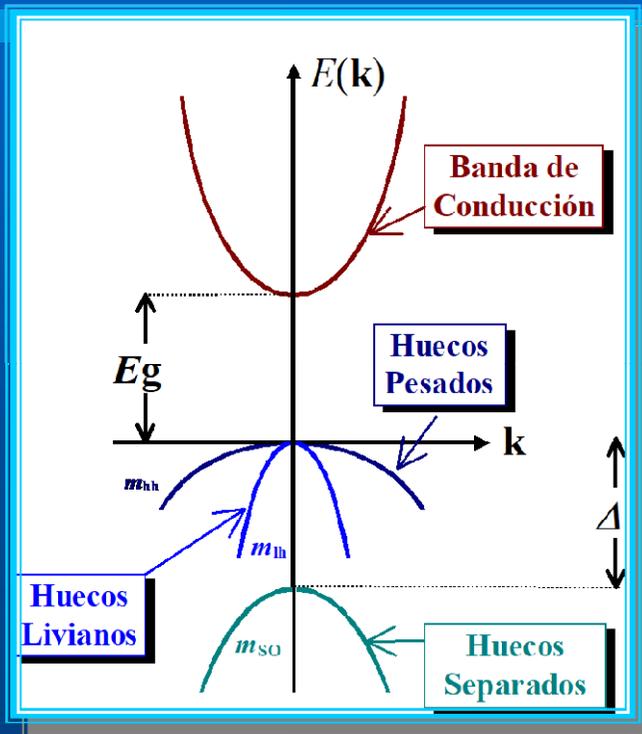
(Hexagonal)

$\Phi$  - "Crystal-Field"

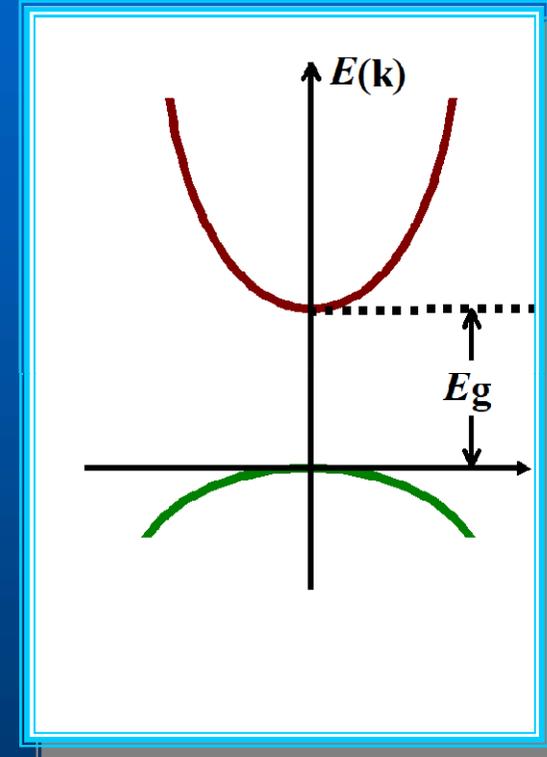
# Origen Atómico de las Bandas



# Absorción Óptica del Borde de Banda



$$E \approx \frac{p^2}{2m}$$



# Propiedades Ópticas de Semiconductores

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# Transiciones Interbanda

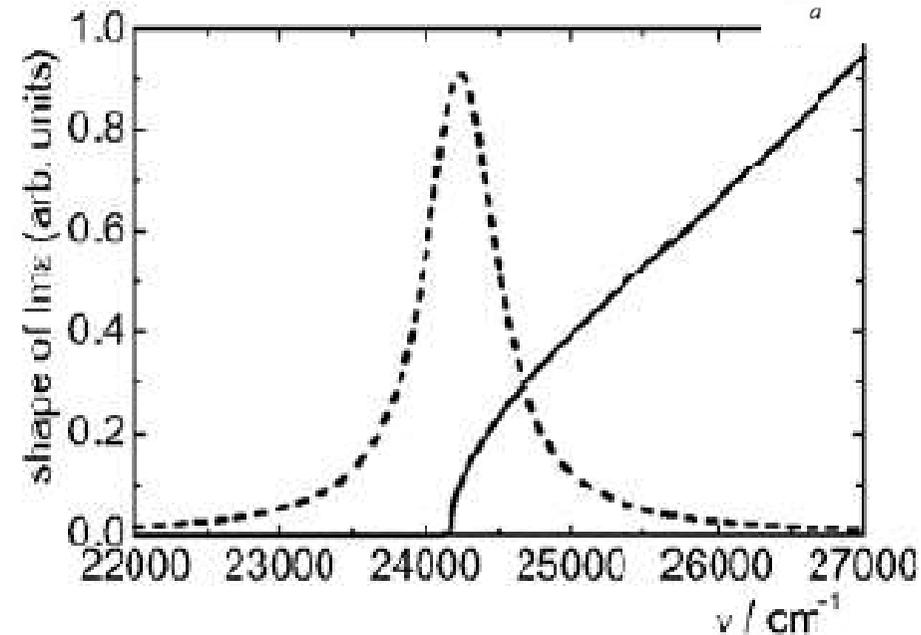
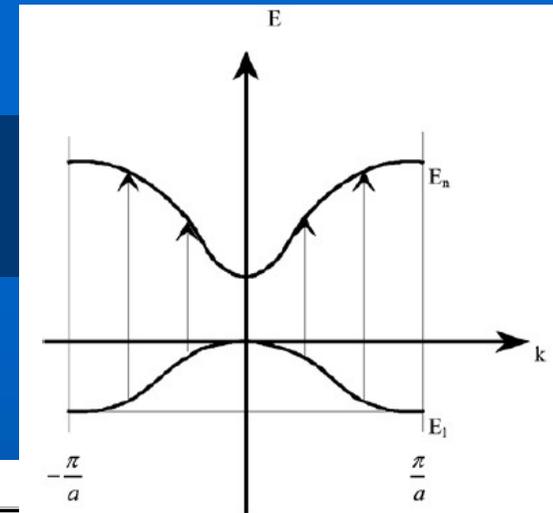


Fig. 12.2. Shape of the imaginary part of the dielectric function as calculated from (12.1) and (12.2), assuming  $E_g = 3 \text{ eV}$ : *solid*:  $B = 1 \text{ eV}$ ,  $\Gamma = 1 \text{ cm}^{-1}$ ; *dash*:  $B = 0.01 \text{ eV}$ ,  $\Gamma = 300 \text{ cm}^{-1}$

# Transiciones Interbanda

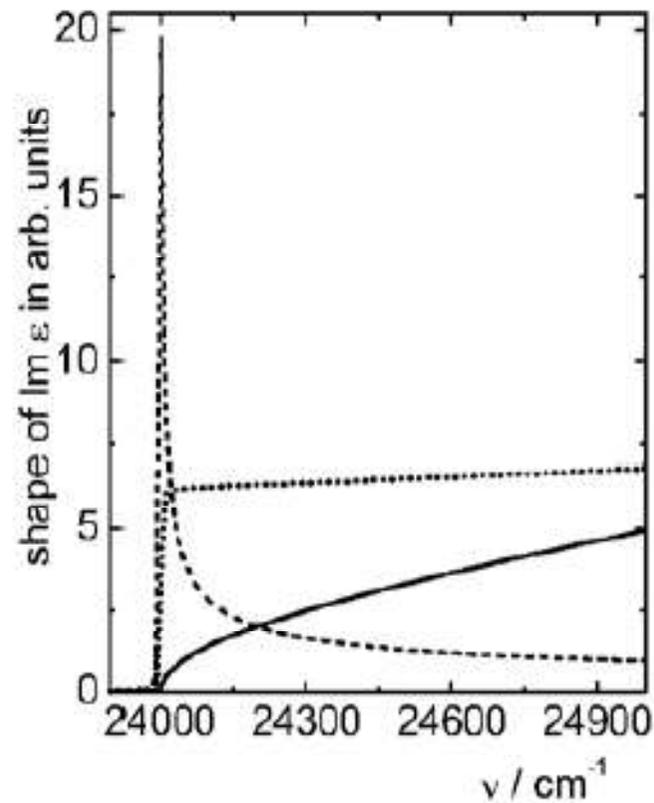


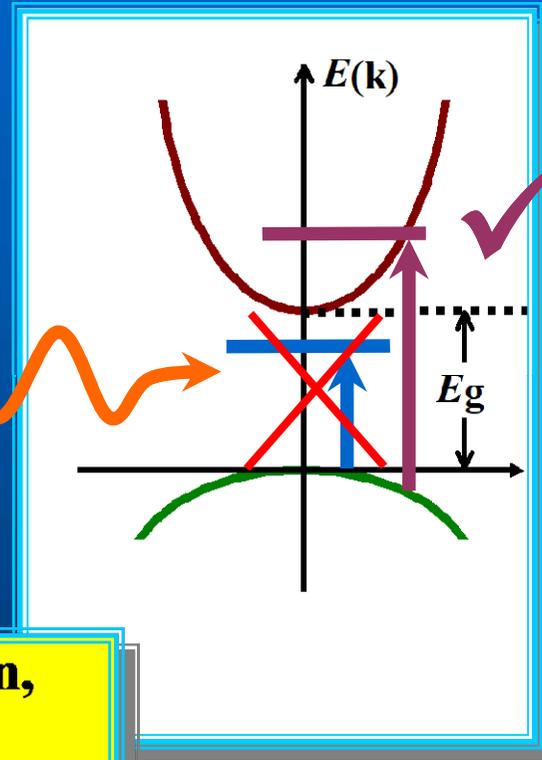
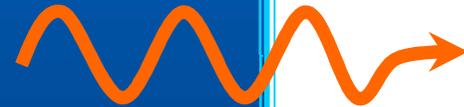
Fig. 12.3. Shape of the imaginary part of the dielectric function in the vicinity of the absorption edge, as calculated from (12.1) and (12.2). *Solid*: 3D; *dot*: 2D; *dash*: 1D.  $E_g = 3\text{ eV}$ ;  $B = 1\text{ eV}$ ;  $\Gamma = 1\text{ cm}^{-1}$

# Absorción Óptica del Borde de Banda

- $h\nu < E_g \Rightarrow \alpha = 0$  ;
- $h\nu > E_g \Rightarrow$

$$\alpha = \frac{2\omega \sum_i q_i}{c}$$

$$E_{ph} = h\nu = \hbar\omega$$



- $\tau^{-1} = 0 \Rightarrow$

$$q_i = f\delta(h\nu - E_i) \rightarrow \text{coeficiente de extinción,}$$

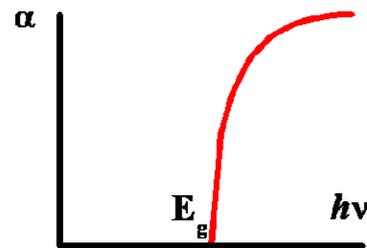
$$\alpha = \frac{2\omega f}{c} \sum_i \delta(h\nu - E_i) \rightarrow \text{coeficiente de absorción,}$$

$$\sum_i \delta(h\nu - E_i) \propto D(h\nu) \rightarrow \text{Densidad de estados}$$

# Absorción Óptica del Borde de Banda

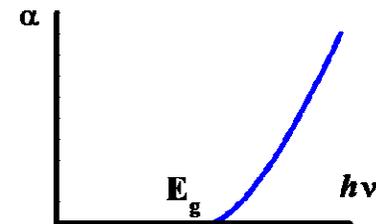
## Gap Directo

$$\alpha \propto \frac{\sqrt{h\nu - E_g}}{h\nu}$$



## Gap Indirecto

$$\alpha \propto \frac{(h\nu - E_g)^2}{h\nu}$$



$$D(h\nu) \propto \sqrt{h\nu - E_g};$$

$$f \propto \frac{1}{(h\nu)^2} \rightarrow \text{Regla de oro de Fermi}$$

➤ Materiales Amorfos  
⇒ Gráficos de “Tauc”.

$$q_i = f\delta(h\nu - E_i) \rightarrow \text{coeficiente de extinción,}$$

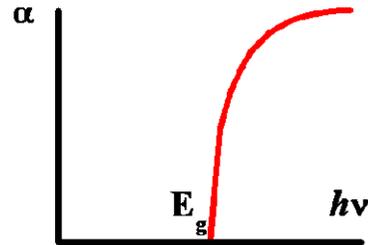
$$\alpha = \frac{2\omega f}{c} \sum_i \delta(h\nu - E_i) \rightarrow \text{coeficiente de absorción,}$$

$$\sum_i \delta(h\nu - E_i) \propto D(h\nu) \rightarrow \text{Densidad de estados}$$

# Bordes de Banda Directos vs. Indirectos

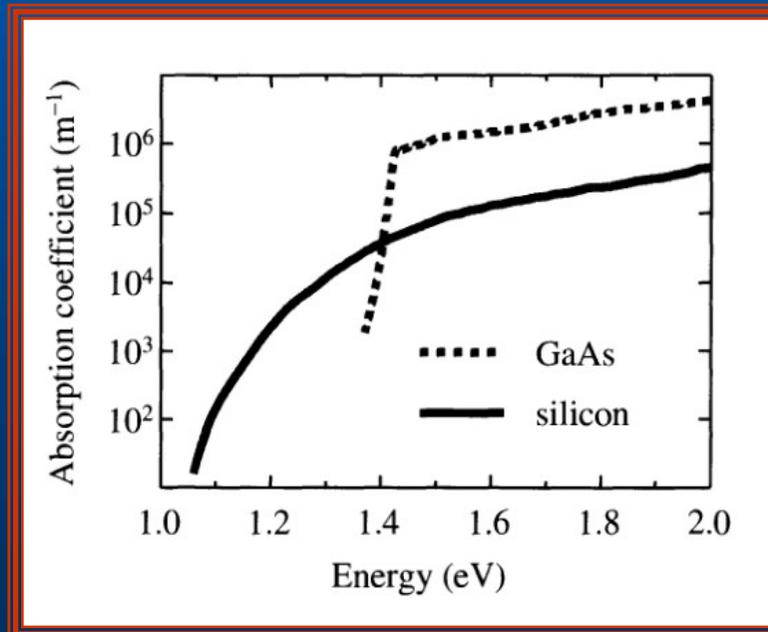
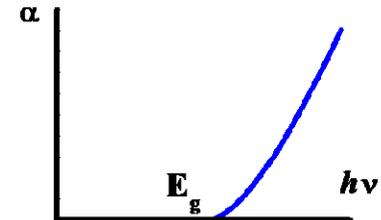
**Gap Directo**

$$\alpha \propto \frac{\sqrt{h\nu - E_g}}{h\nu}$$



**Gap Indirecto**

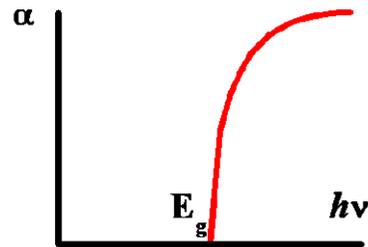
$$\alpha \propto \frac{(h\nu - E_g)^2}{h\nu}$$



# Búsqueda de Bordos Directos e Indirectos

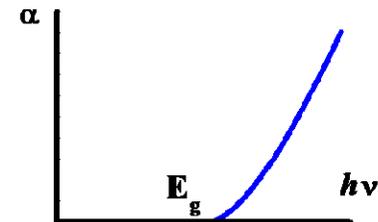
## Gap Directo

$$\alpha \propto \frac{\sqrt{h\nu - E_g}}{h\nu}$$



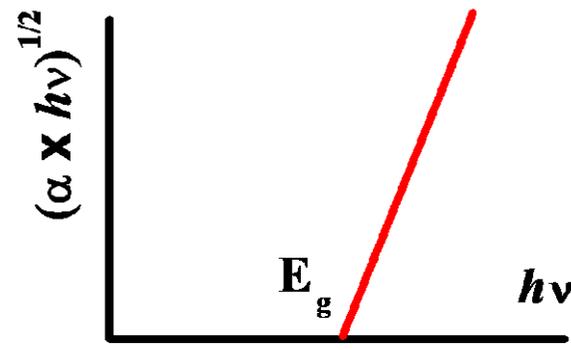
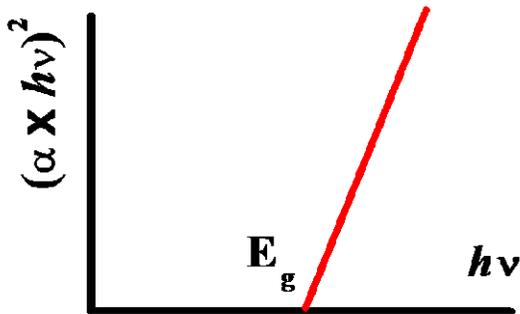
## Gap Indirecto

$$\alpha \propto \frac{(h\nu - E_g)^2}{h\nu}$$

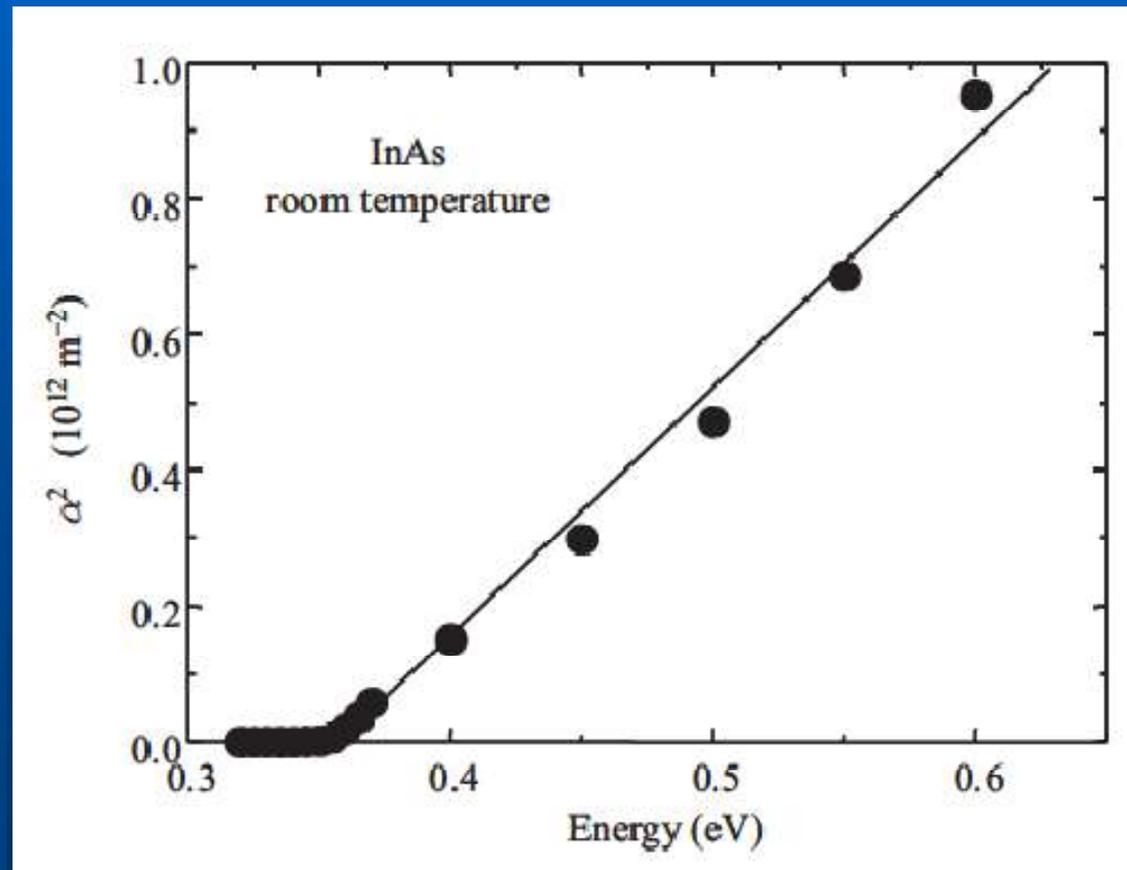


$$(\alpha \times h\nu)^2 \propto h\nu - E_g$$

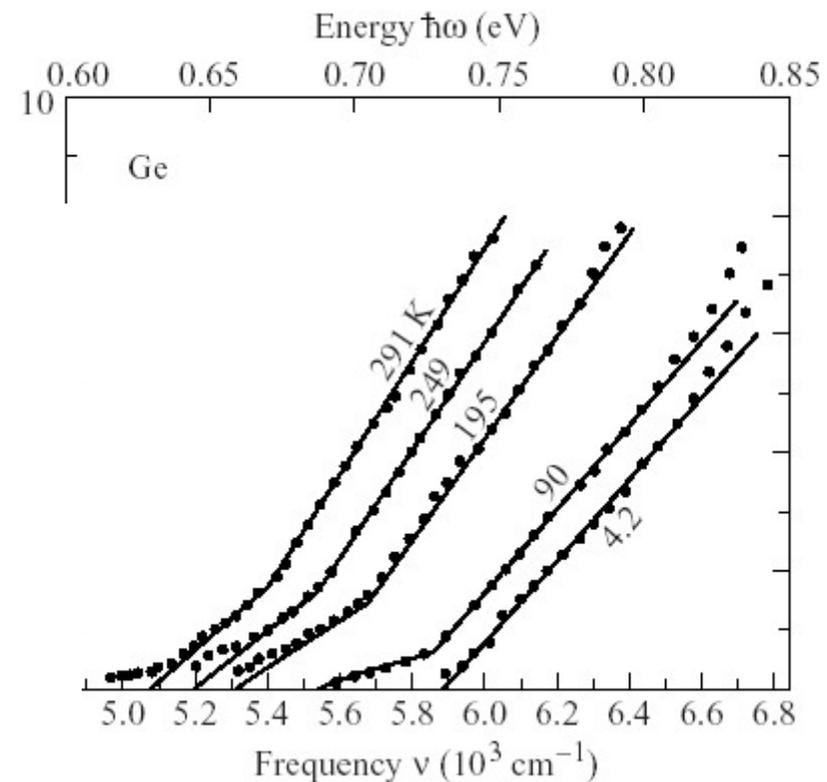
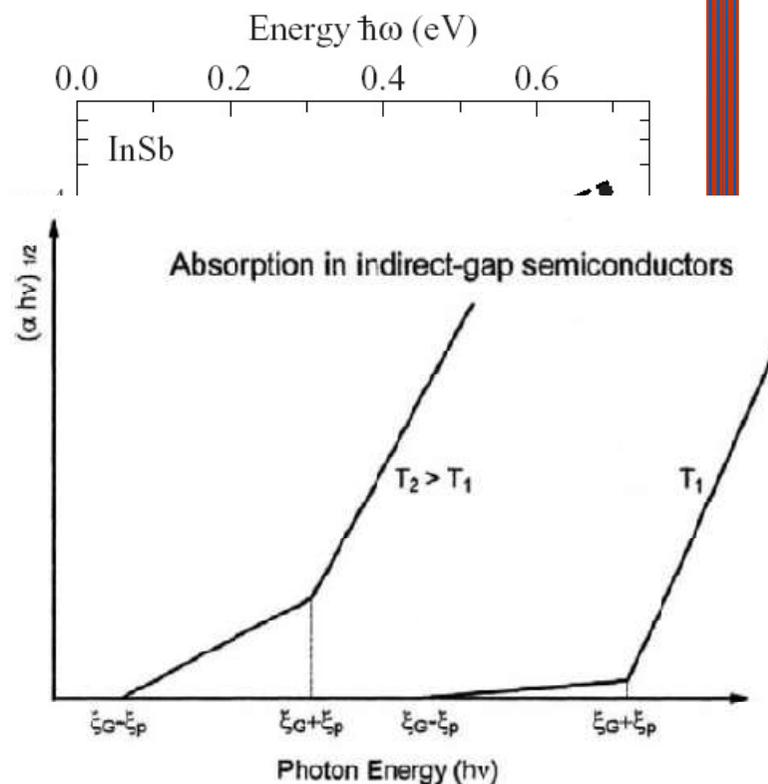
$$\sqrt{\alpha \times h\nu} \propto h\nu - E_g$$



# Borde de Absorción Directo (InAs)

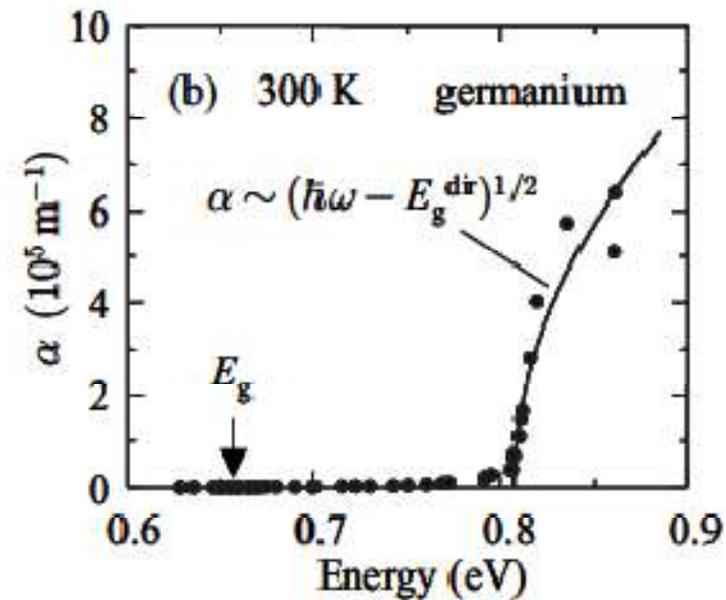
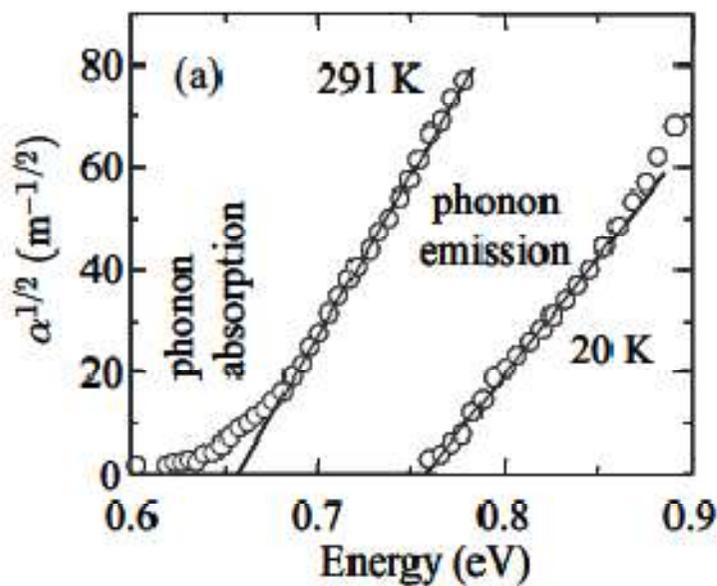
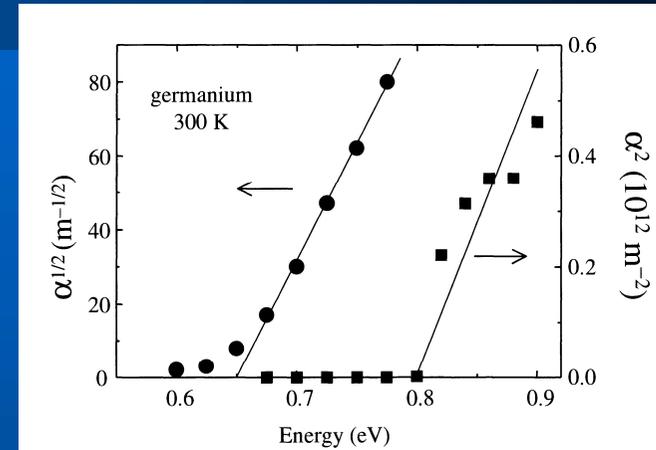
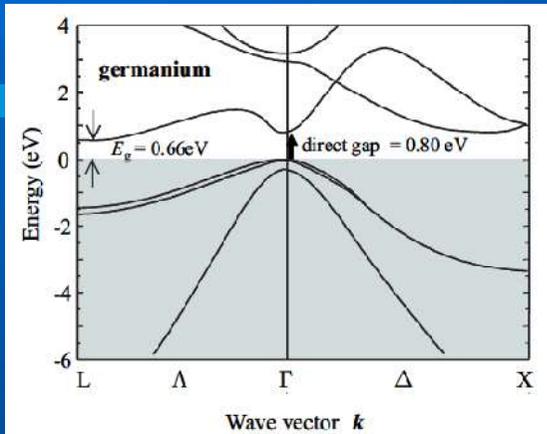


# Superposición de Bordes

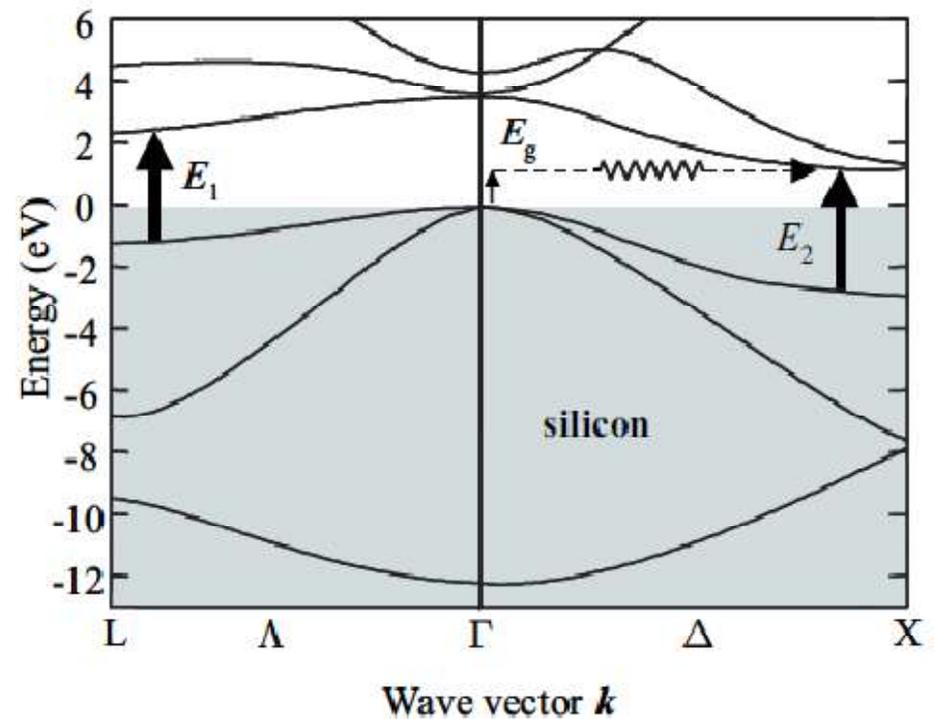
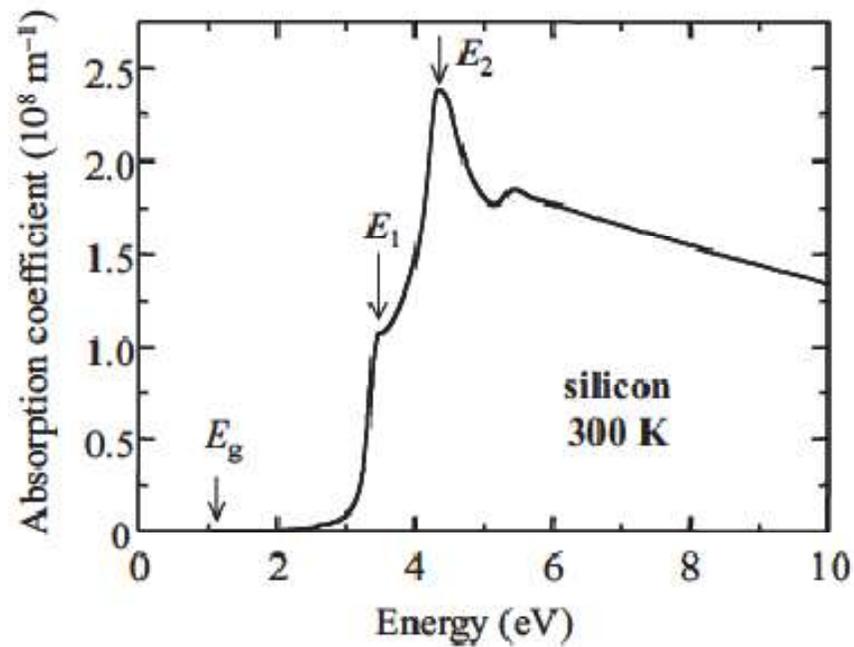


**Figure 5.12:** Typical absorption behavior for an indirect-gap semiconductor. At low energy, only phonon absorption can mediate the electron excitation. As the temperature is lowered, the smaller phonon population decreases the absorption probability, as shown.

# Superposición de Bordos (Ge)



# Superposición de Bordos (Si)

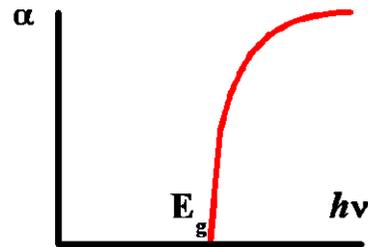




# Búsqueda de Bordos Directos e Indirectos

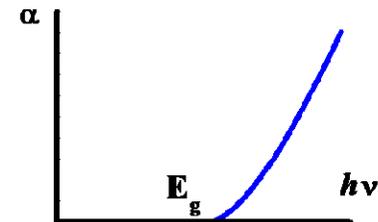
## Gap Directo

$$\alpha \propto \frac{\sqrt{h\nu - E_g}}{h\nu}$$



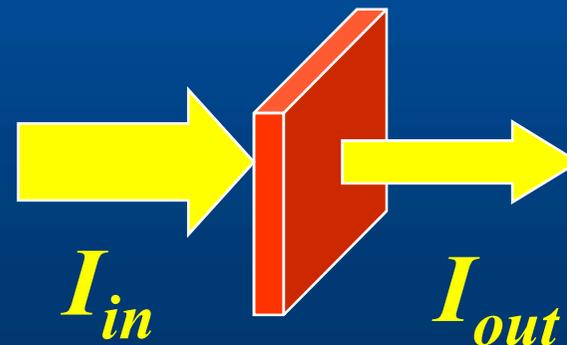
## Gap Indirecto

$$\alpha \propto \frac{(h\nu - E_g)^2}{h\nu}$$



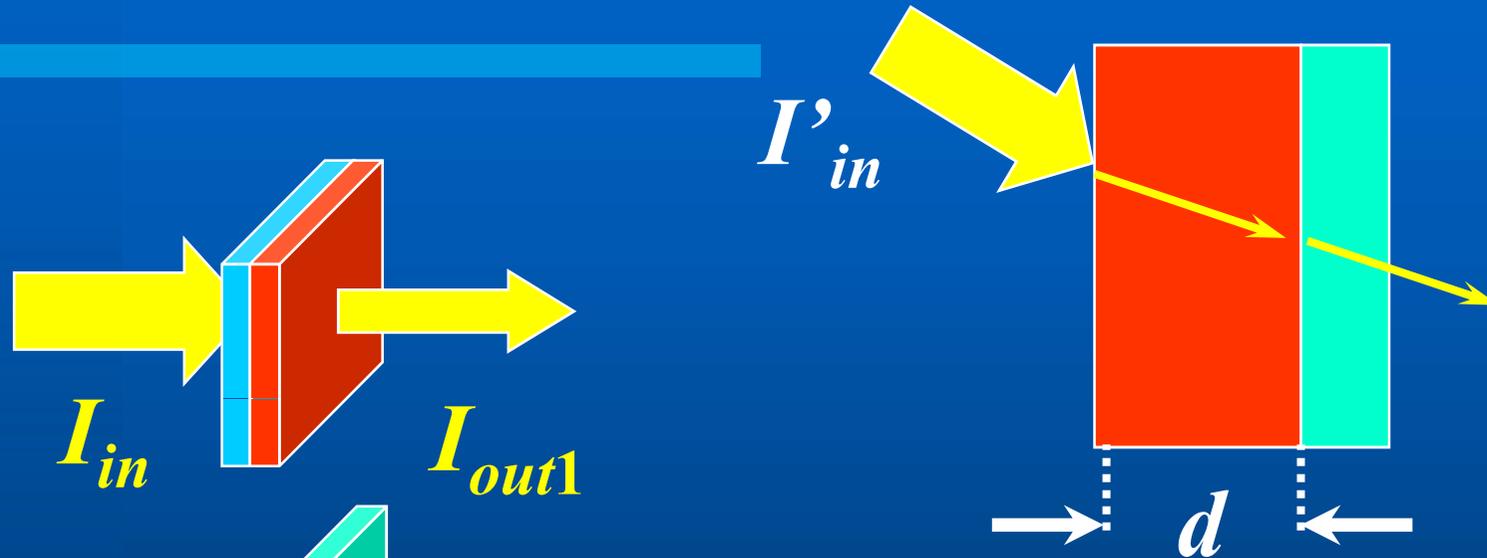
$$\text{Transmitancia: } T = \frac{I_{out}}{I_{in}}$$

$$\text{Coeficiente de Absorción: } \alpha \propto -\ln T$$



$h\nu = hc/\lambda \rightarrow$  Energía del Fotón  
 $\lambda \rightarrow$  Longitud de Onda

# Transmitancia: Substrato Transparente

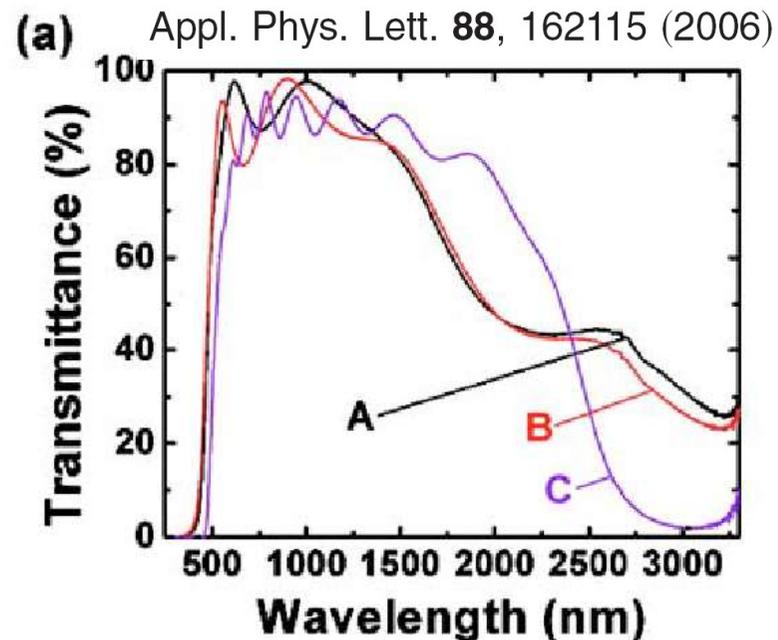


**Transmitancia total:**  $T_{total} = \frac{I_{out1}}{I_{in}}$

**Transmitancia substrato:**  $T_{subst} = \frac{I_{out2}}{I_{in}}$

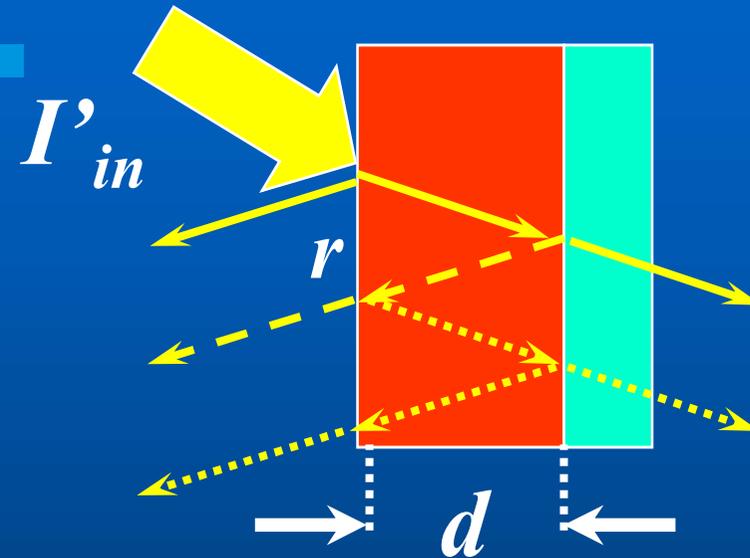
**Transmitancia del film:**  $T_{film} = \frac{I_{out1}}{I_{out2}}$

# Transmitancia: Substrato Transparente



$$T \approx (1 - r) \exp(-\alpha d)$$

$$\Rightarrow \alpha \approx -\ln T$$

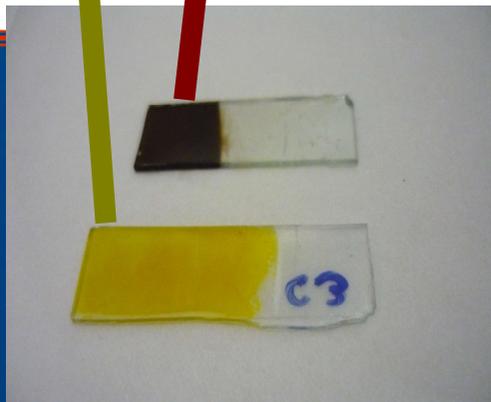
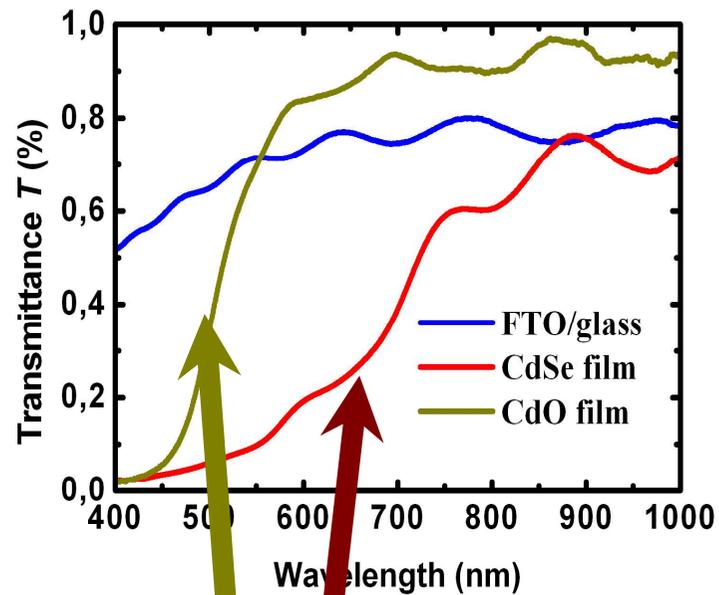


➤ Películas muy finas:  
Interferencia

➤  $n$ :

$$n = \frac{1}{\left( \frac{1}{\lambda_{max1}} - \frac{1}{\lambda_{max2}} \right) 2d}$$

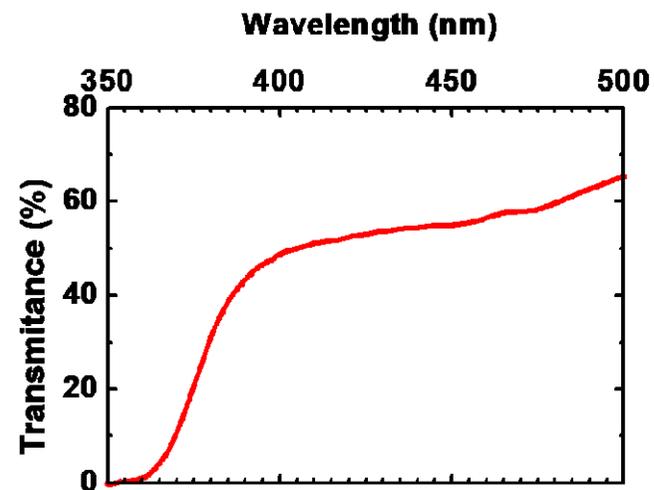
# Influencia del Sustrato



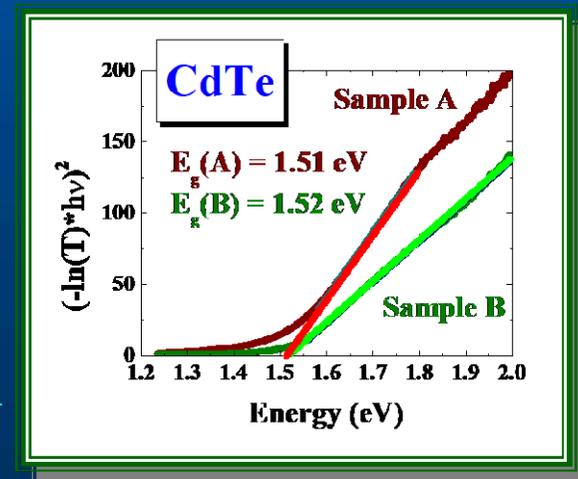
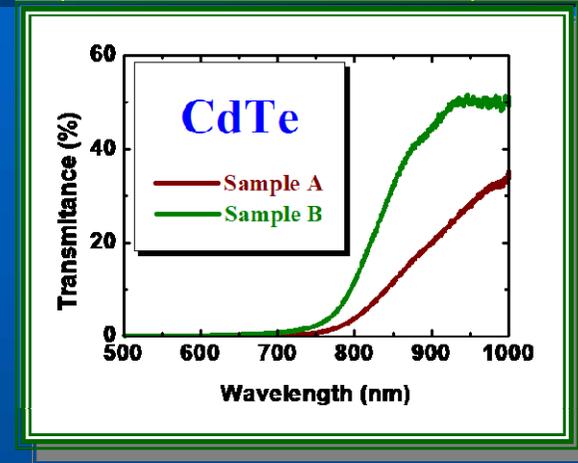
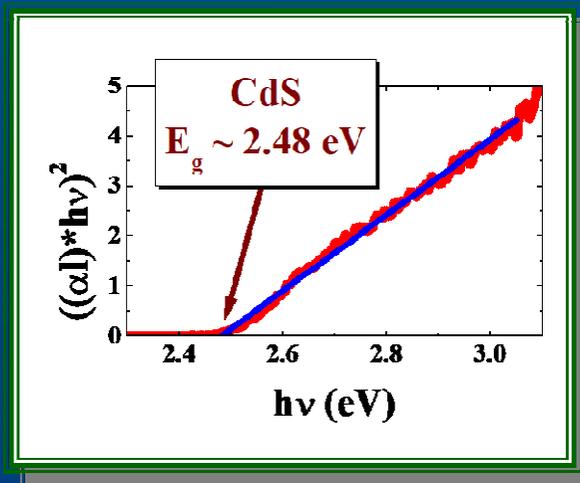
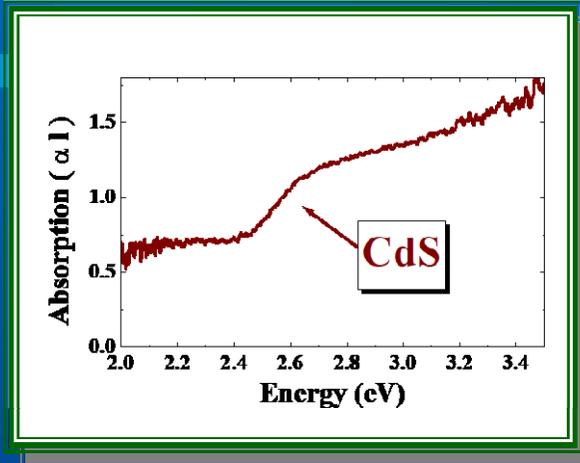
II VI

	B	C	N	O	
	Al	Si	P	S	
Cu	Zn	Ga	Ge	As	Se
Ag	Cd	In	Sn	Sb	Te
Au	Hg	Tl	Pb	Bi	Po

Diagram illustrating the periodic table with elements II, VI, Zn, Cd, and O highlighted. Arrows indicate the relationship between these elements and the films shown in the graph.



# CdX (X=S, Te)



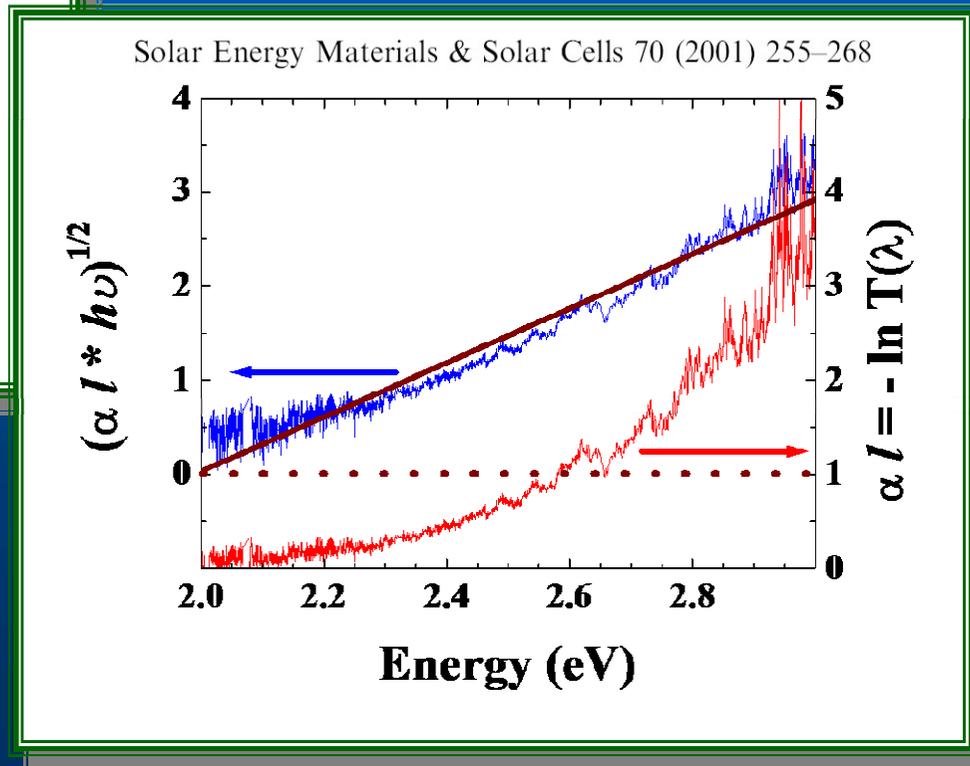
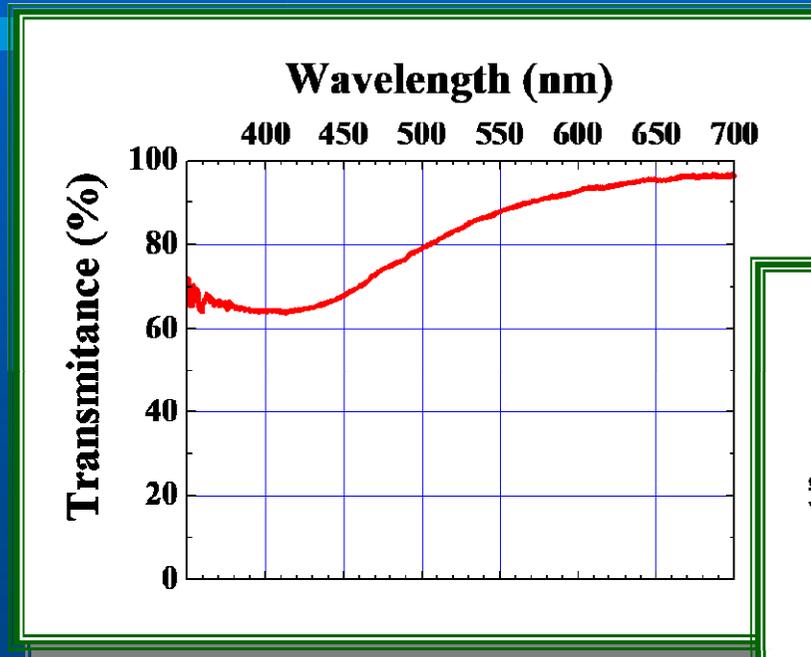
Chemical

Bath

Deposition

# “Red” Selenium

Selenium in excess tend to remain as Amorphous “Red” Selenium.



“Indirect”

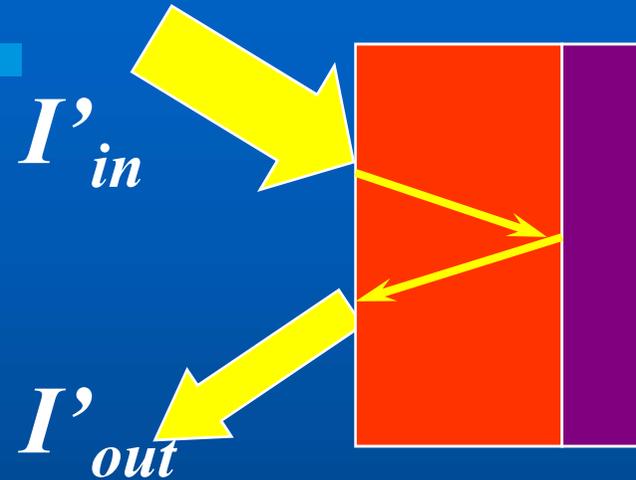
$$E_g = 2.0 \text{ eV} \Rightarrow$$

# Substrato Opaco

- Un método:

$$\text{Reflectancia: } R = \frac{I'_{out}}{I'_{in}}$$

$$\alpha(h\nu) \propto \ln\left(\frac{R_{max} - R_{min}}{R(h\nu) - R_{min}}\right)$$



$\lambda \rightarrow$  Longitud de Onda

$$\lambda_g = hc/E_g$$

- Más “fácil”:

*Gap Directo*

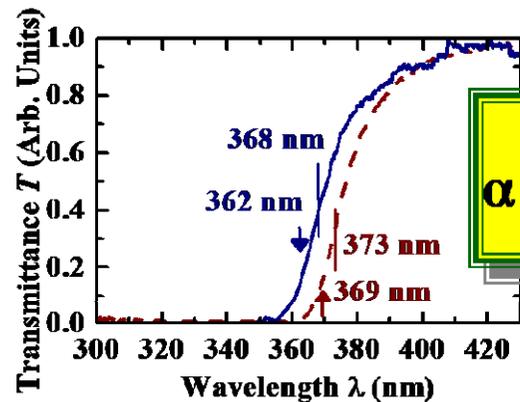
$$\frac{dR}{d\lambda}(\lambda_g) \rightarrow \infty$$

*Gap Indirecto*

$$\frac{dR}{d\lambda}(\lambda_g) \rightarrow 0$$

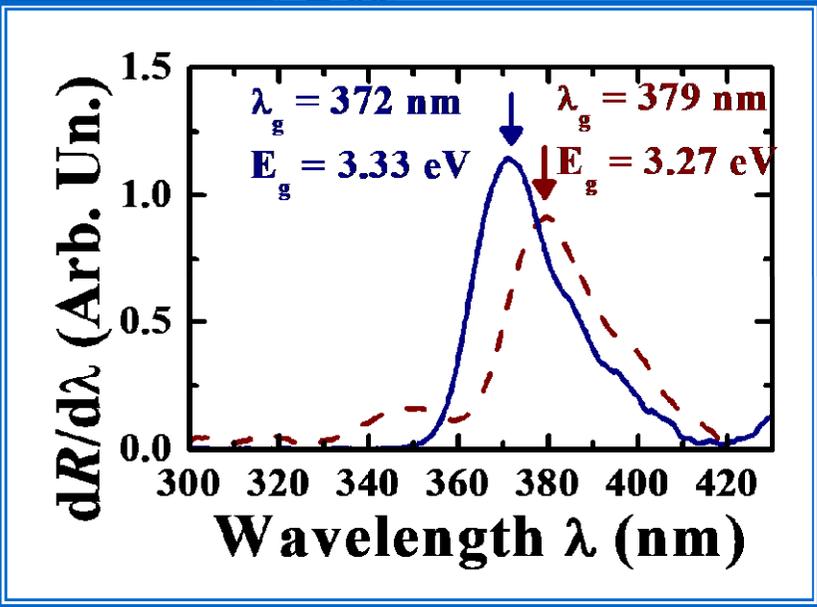
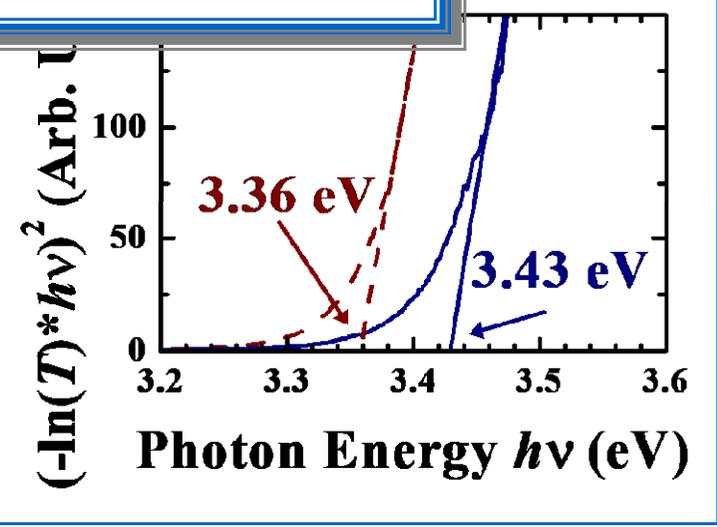
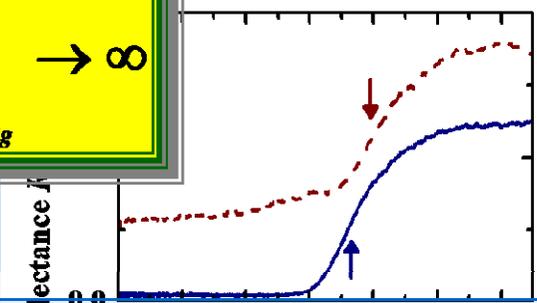
# Transmittance vs Reflectance (for direct semiconductors)

Solar Energy Materials and Solar Cells 82, 85 – 103 (2004).

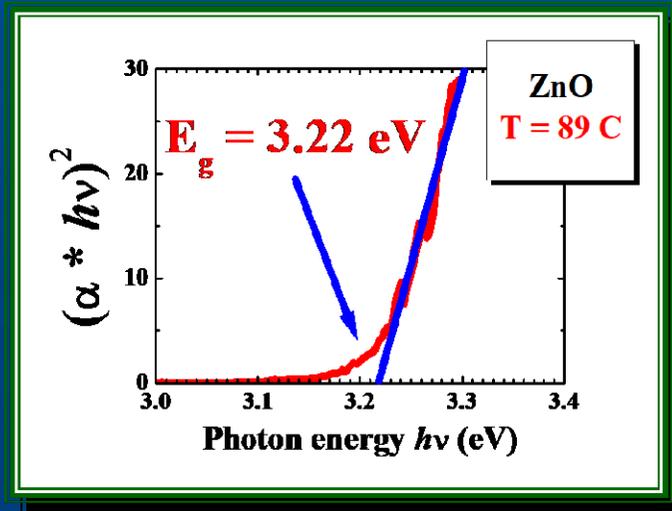
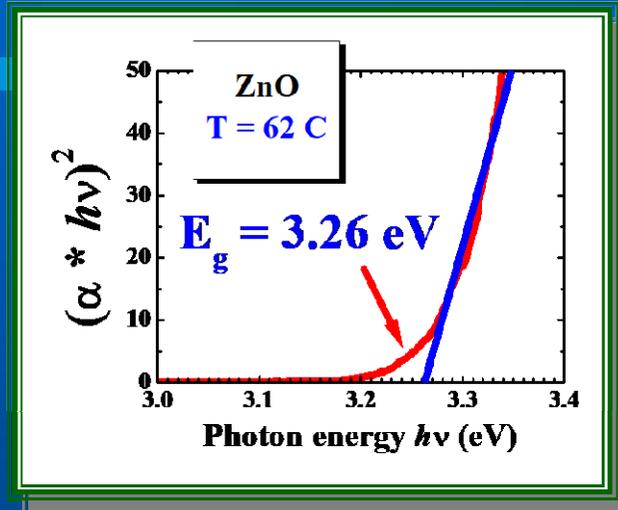


$$\alpha \propto -\ln T \propto \frac{\sqrt{h\nu - E_g}}{h\nu}$$

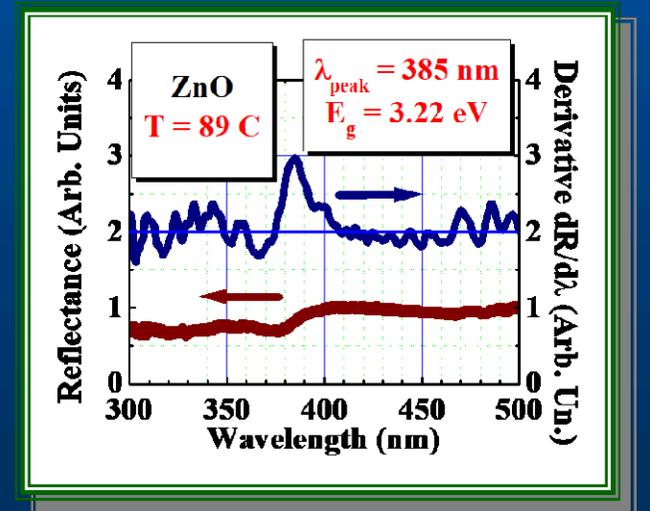
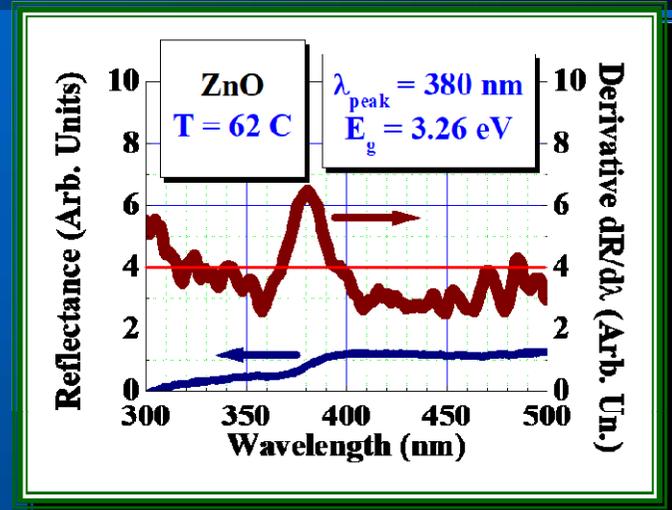
$$\left. \frac{dR(\lambda)}{d\lambda} \right|_{\lambda_g} \rightarrow \infty$$



# ZnO/Cu

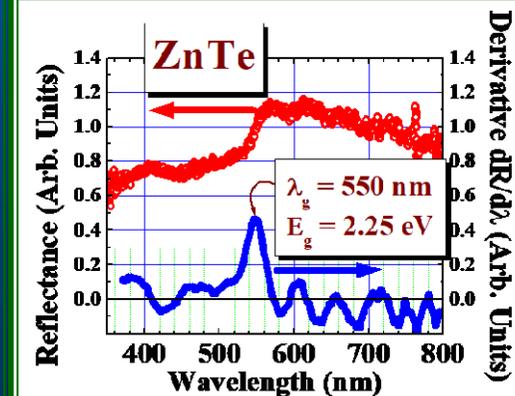
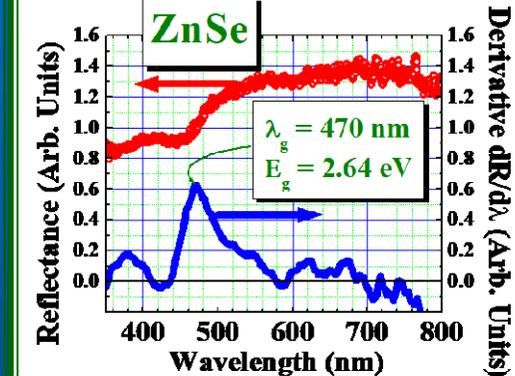
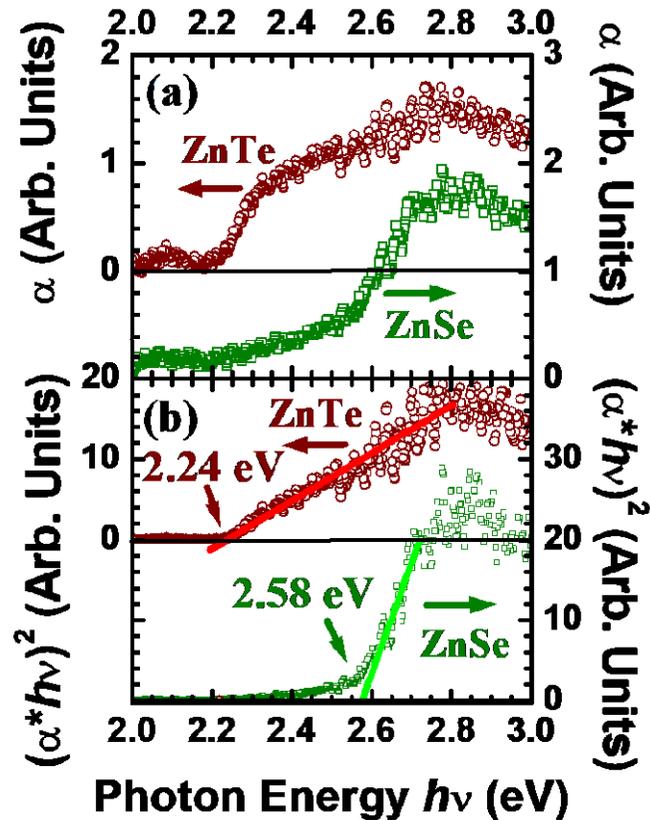


Electro-chemically deposited ZnO onto Copper Opaque Substrates (T is for Deposition Temperature)

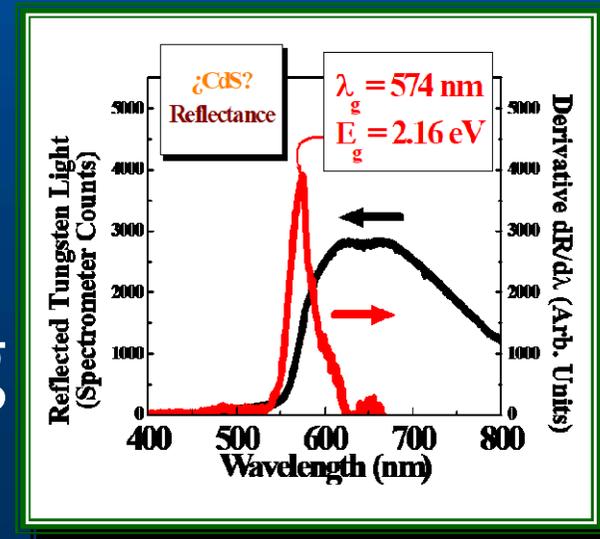
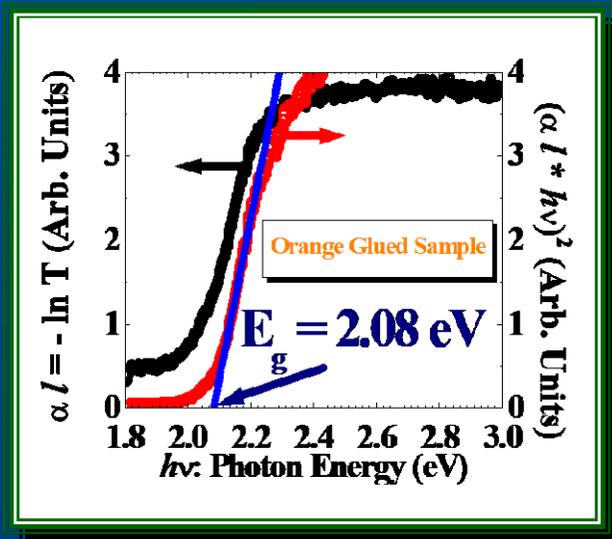
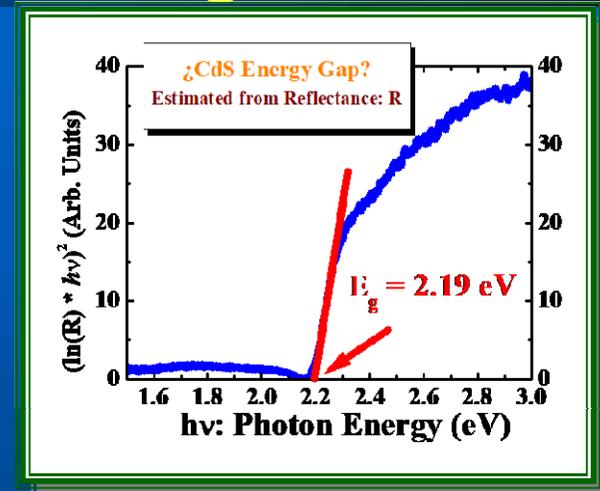
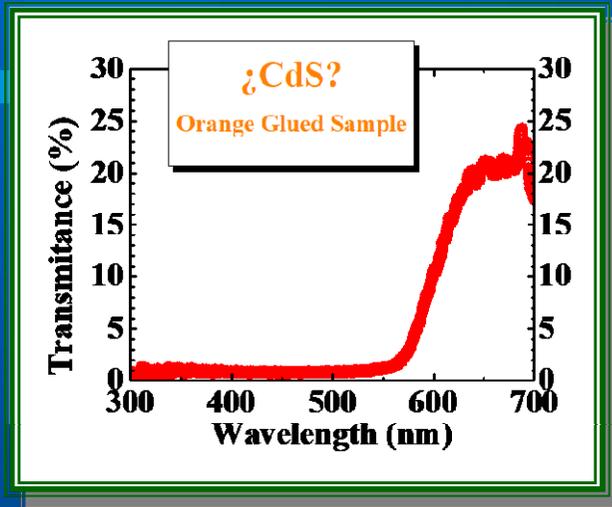


# ZnX (X=Se, Te)

Electro-chemically deposited ZnSe and ZnTe onto Titanium Opaque Substrates



# ¿CdS?



# Silk

# Screen

# Printing

# Resumen

Material	Color	Accepted $E_g$ (eV) (T = 300K)	Measured $E_g$ (eV) (T = 300K)
ZnO	white- translucent	3.2 – 3.4	3.3
ZnSe	yellow-brownish	2.67	2.64
ZnTe	coffee	2.26	2.25
CdS	yellow	2.42	2.48
CdTe	black	1.49	1.51

Properties of  
Wide Bandgap II-VI Semiconductors  
Ed. Rameshwar Bhargava.  
EMIS Datareviews Series (1997).

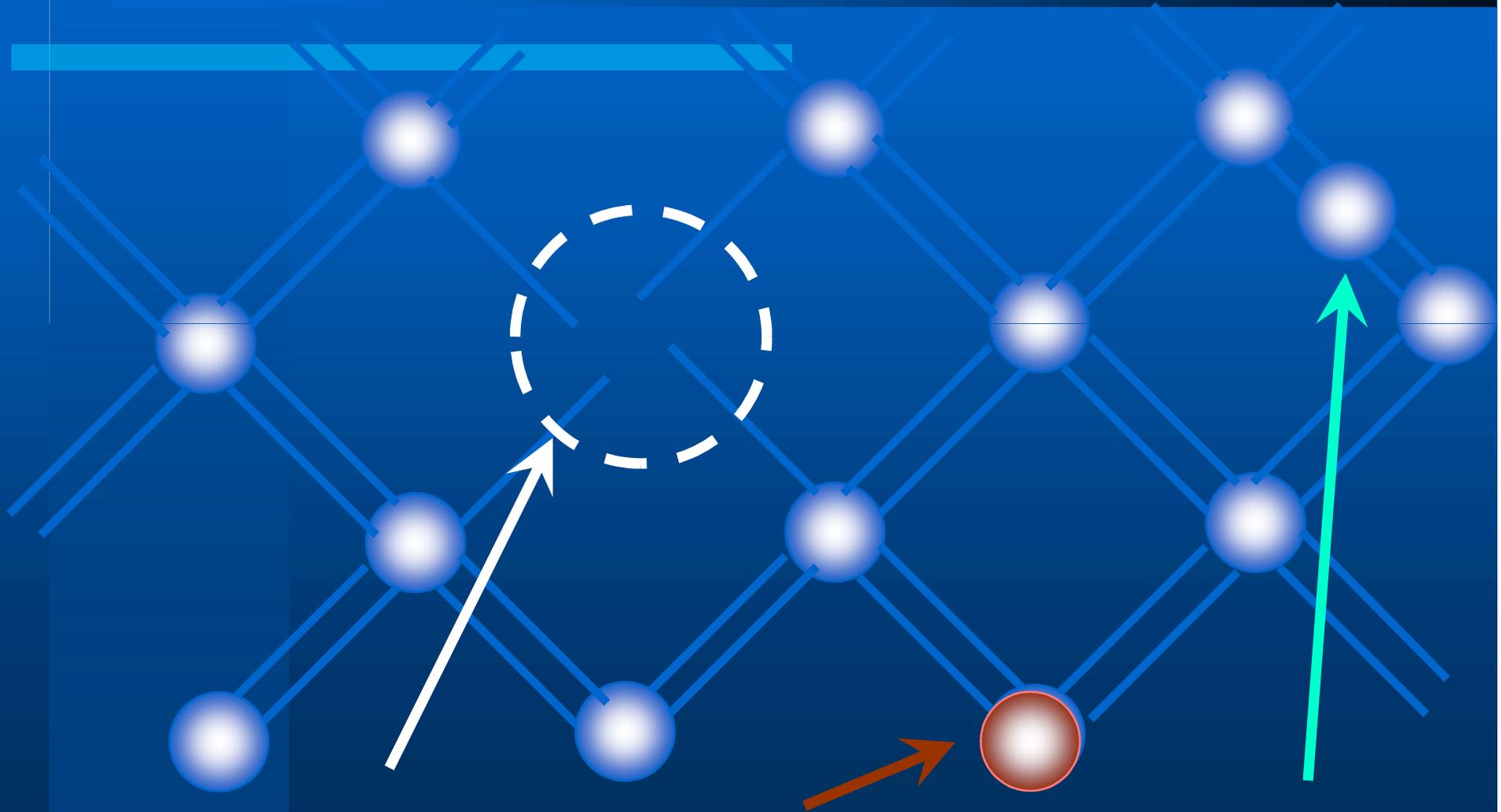
# Propiedades Ópticas de Semiconductores

- Estructura Electrónica
- **Absorción Óptica en Semiconductores**
- Influencia de Defectos
- Excitones
- Efectos Nanométricos

# Propiedades Ópticas de Semiconductores

- Estructura Electrónica
- Absorción Óptica en Semiconductores
- **Influencia de Defectos**
- **Excitones**
- Efectos Nanométricos

# Defectos



• Vacancias

• Impurezas

• Intersticiales

# Resistividad Eléctrica

$$\rho = \frac{m_e}{ne^2\tau}$$

- $m_e$ : Masa Efectiva Electrónica (Teoría de Bandas).
- $n$ : Densidad de **Electrones de Conducción** (o **Huecos**)
  - Metales**: aprox. constante.
  - Semiconductores**: Fuertemente Dependiente (ej: **Impurezas**)
- $\tau$ : Tiempos de Relajación:

**Colisiones → Pérdidas de Energía.**

# Resistividad en Semiconductores

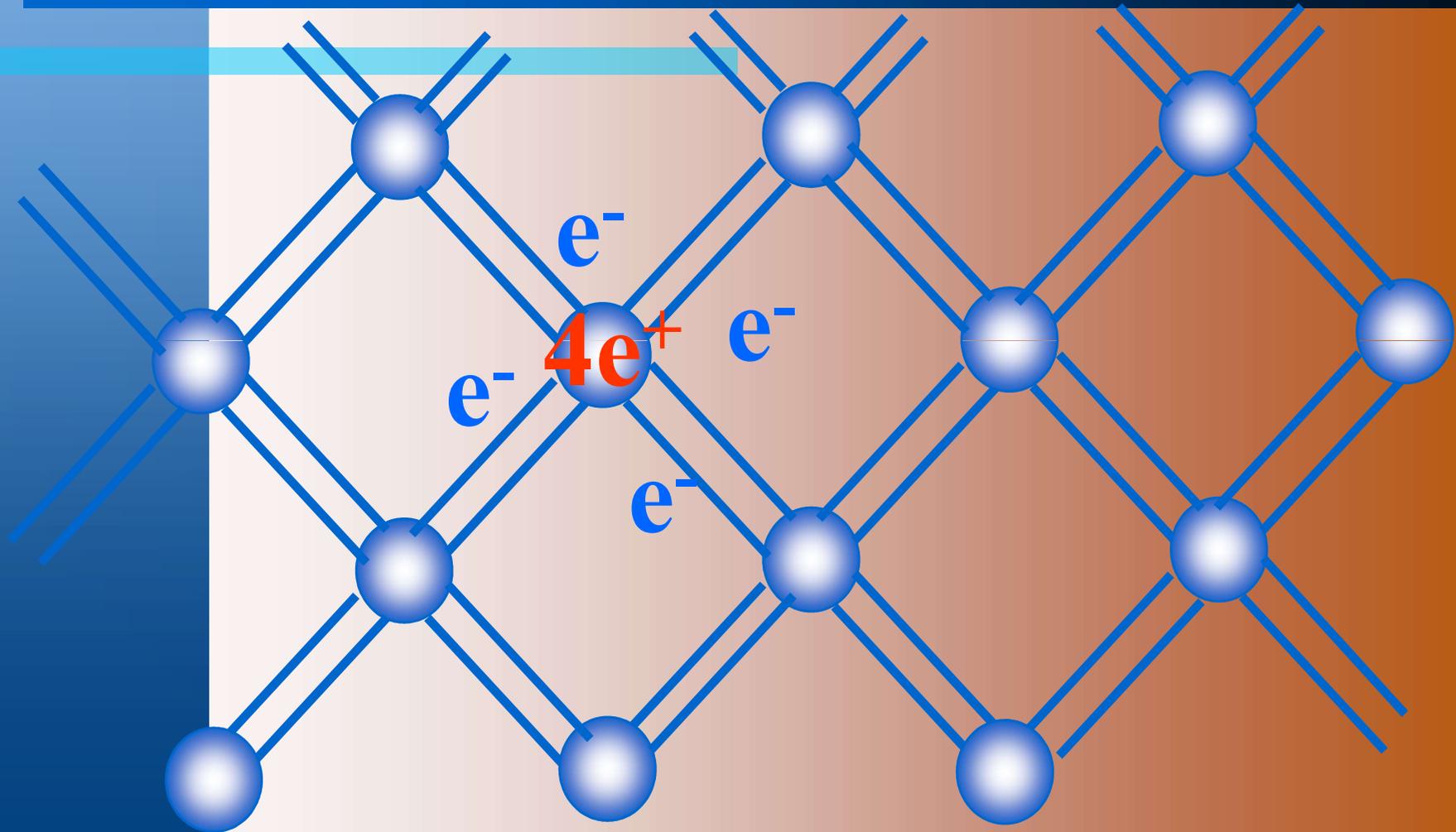
$$\sigma = \frac{1}{\rho} = e^2 \left( \frac{n\tau_e}{m_e} + \frac{p\tau_p}{m_p} \right)$$

Electrones  
de Conducción

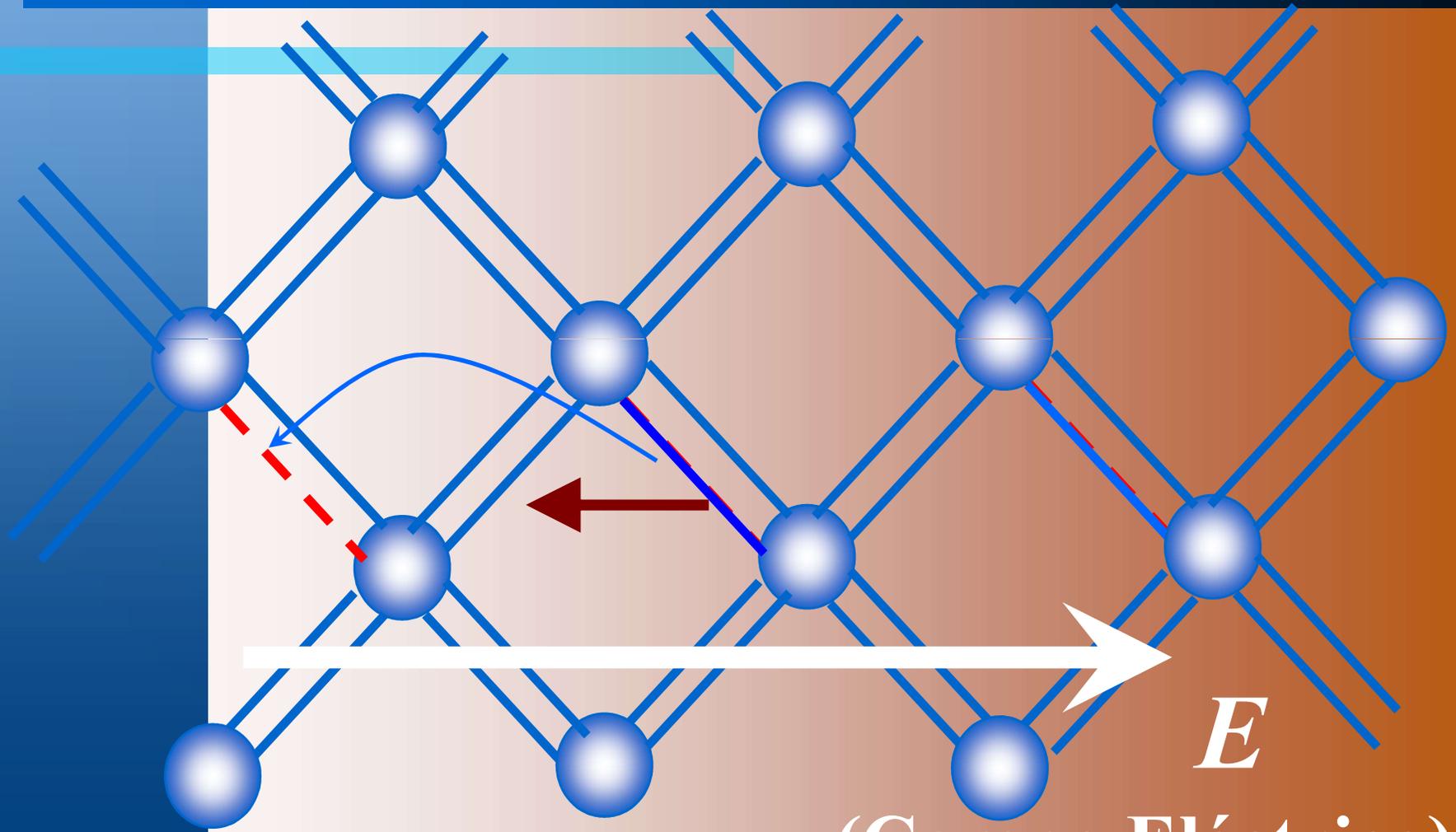
Huecos

Estados Libres de la Banda de Valencia

# El Hueco “Químico”

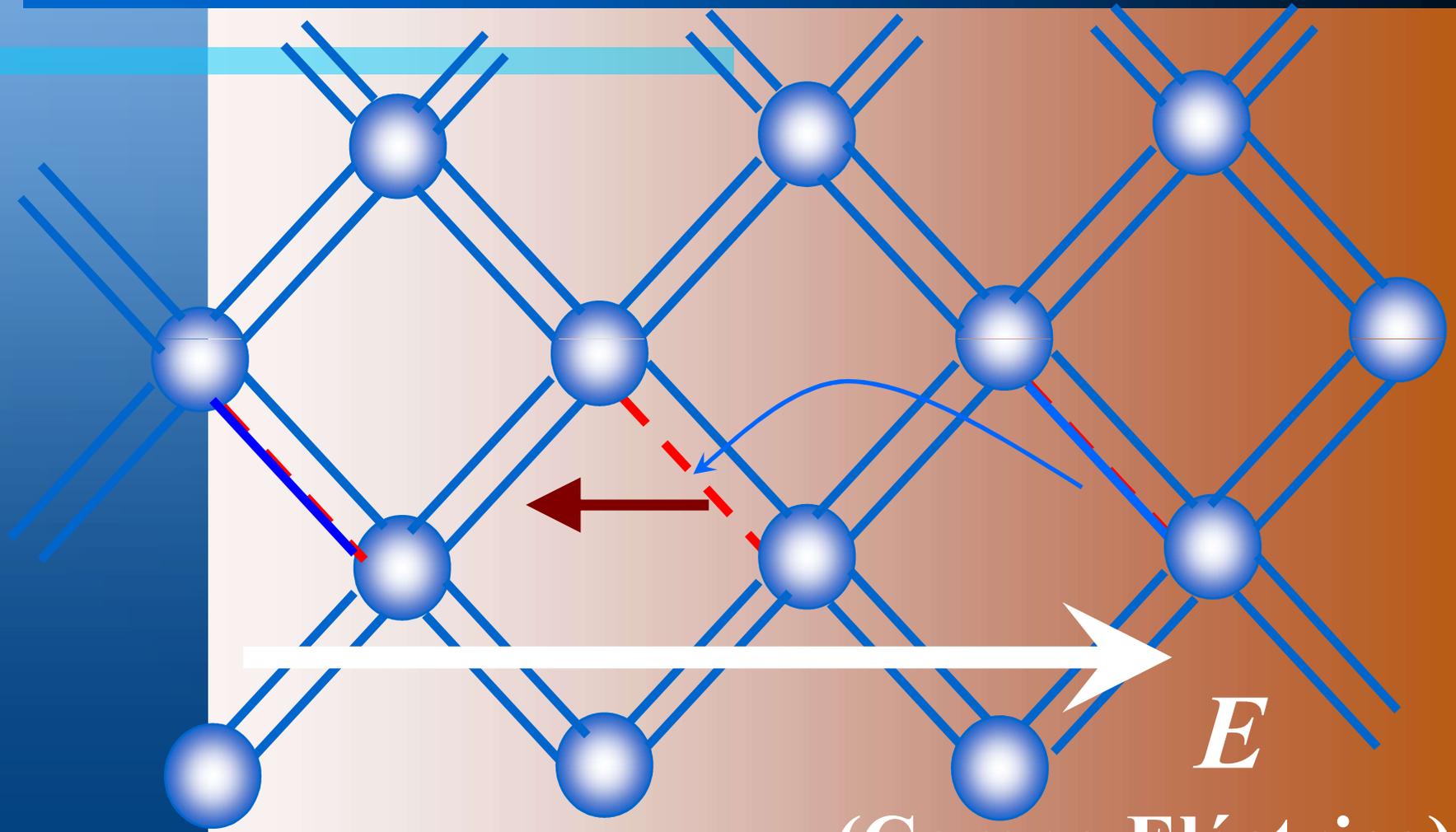


# El Hueco “Químico”



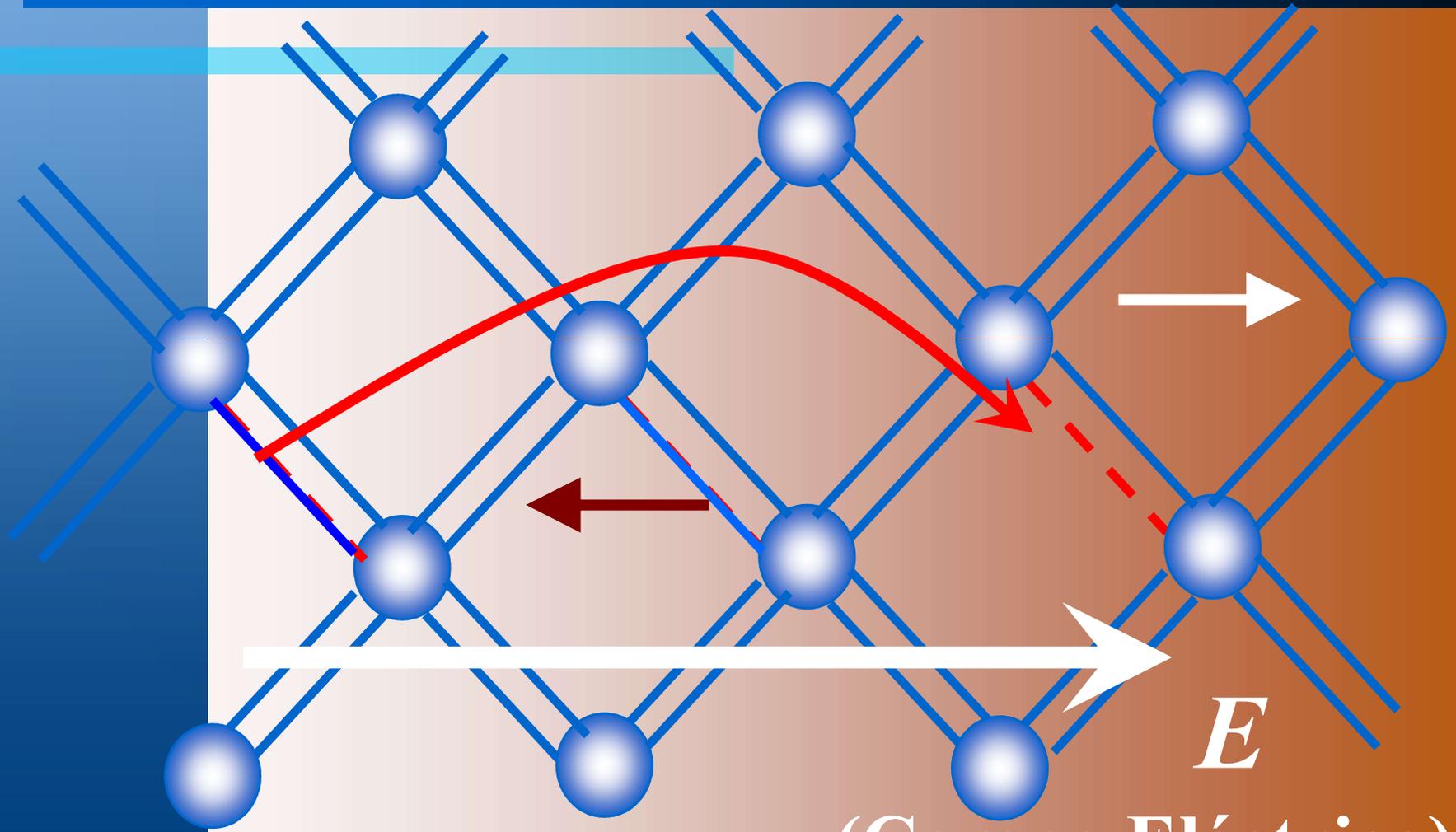
(Campo Eléctrico)

# El Hueco “Químico”



(Campo Eléctrico)

# El Hueco “Químico”



(Campo Eléctrico)

# Resistividad Eléctrica

$$\rho = \frac{m_e}{ne^2\tau}$$

- $m_e$ : Masa Efectiva Electrónica (Teoría de Bandas).
- $n$ : Densidad de **Electrones de Conducción** (o **Huecos**)

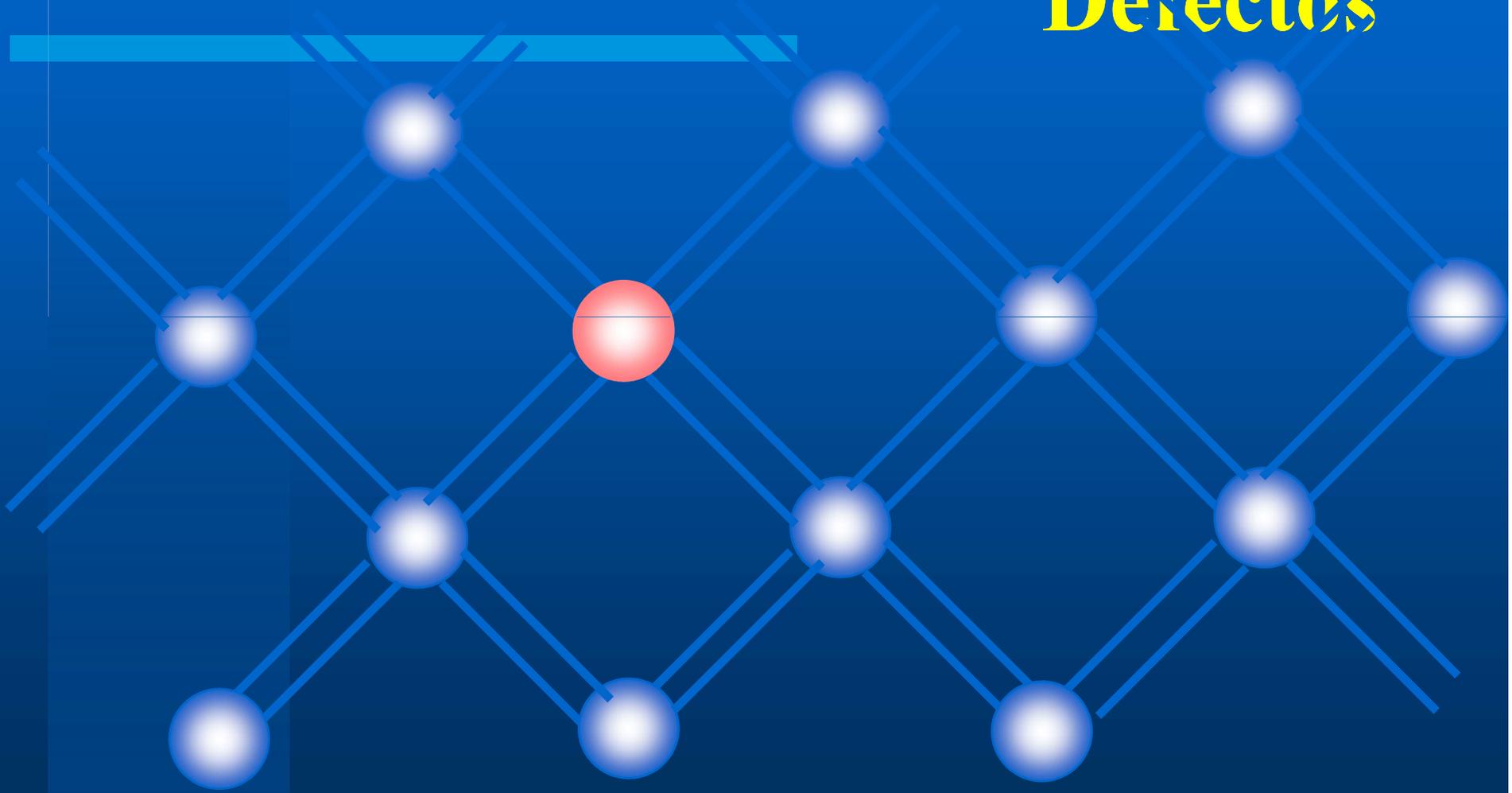
**Metales:** aprox. constante.

**Semiconductores:** Fuertemente Dependiente (ej: **Impurezas**)

- $\tau$ : Tiempos de Relajación:

**Colisiones → Pérdidas de Energía.**

# Propiedades Electrónicas de Defectos



# Propiedades Electrónicas de Defectos

Cristal Perfecto:

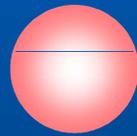
$\vec{\mathbf{R}}$ :  
Red de Bravais

$$V(\vec{\mathbf{r}}) = V(\vec{\mathbf{r}} + \vec{\mathbf{R}})$$

Número de  
Átomos en el Cristal

$$= \sum_i^N V_{1 \text{ atom}}(\vec{\mathbf{r}} - \vec{\mathbf{R}}_i)$$

# Propiedades Electrónicas de Defectos



Impurity:

$$V_{imp} \left( \begin{matrix} \vec{r} \\ \mathbf{r} \end{matrix} \right)$$

# Propiedades Electrónicas de Defectos

Cristal Perfecto:

$$V(\vec{\mathbf{r}}) - V_{1 \text{ atom}}(\vec{\mathbf{r}})$$

Cristal con una impureza:

Impureza:

$$V_{imp}(\vec{\mathbf{r}})$$

$$\Delta V = V_{imp}(\vec{\mathbf{r}}) - V_{1 \text{ atom}}(\vec{\mathbf{r}})$$

# Defectos en Semiconductores

- **“Shallow” Impurities:**

(Impurezas Hidrogenoides)

- Propiedades similares que en el **Átomo de Hidrógeno**: dependen fuertemente de la estructura electrónica de bandas.

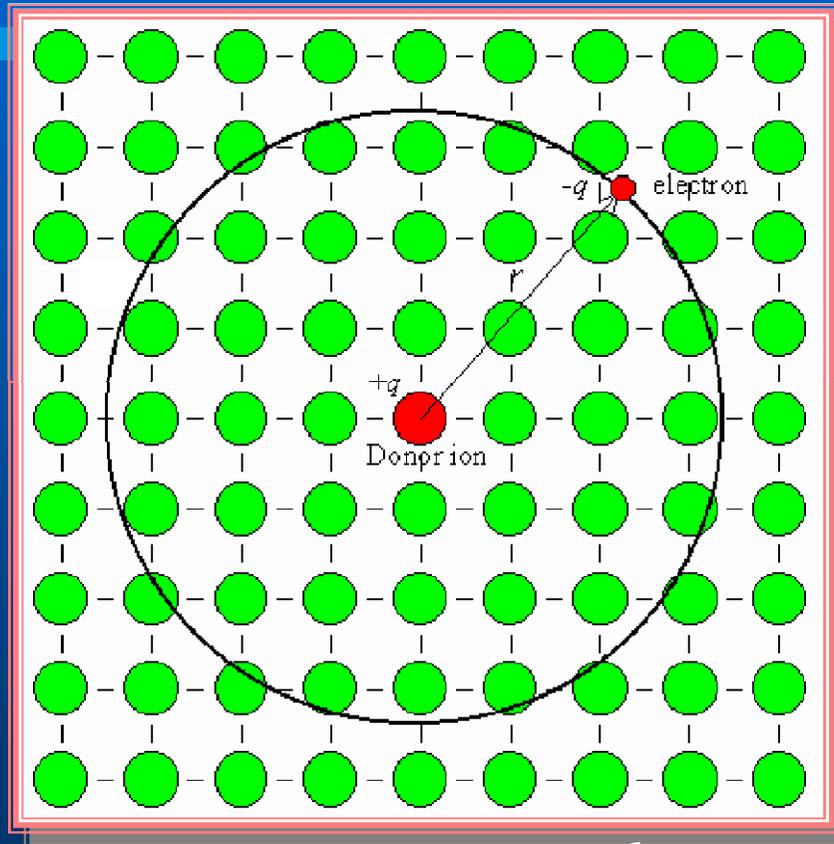
- **Deep Centers:**

(Not shallow)

- Definidos usualmente como estados que se encuentran ubicados profundamente (“deep”) dentro del gap.
- Estados altamente localizados.
- Deformaciones cristalinas deben incluirse en  $\Delta V$ .

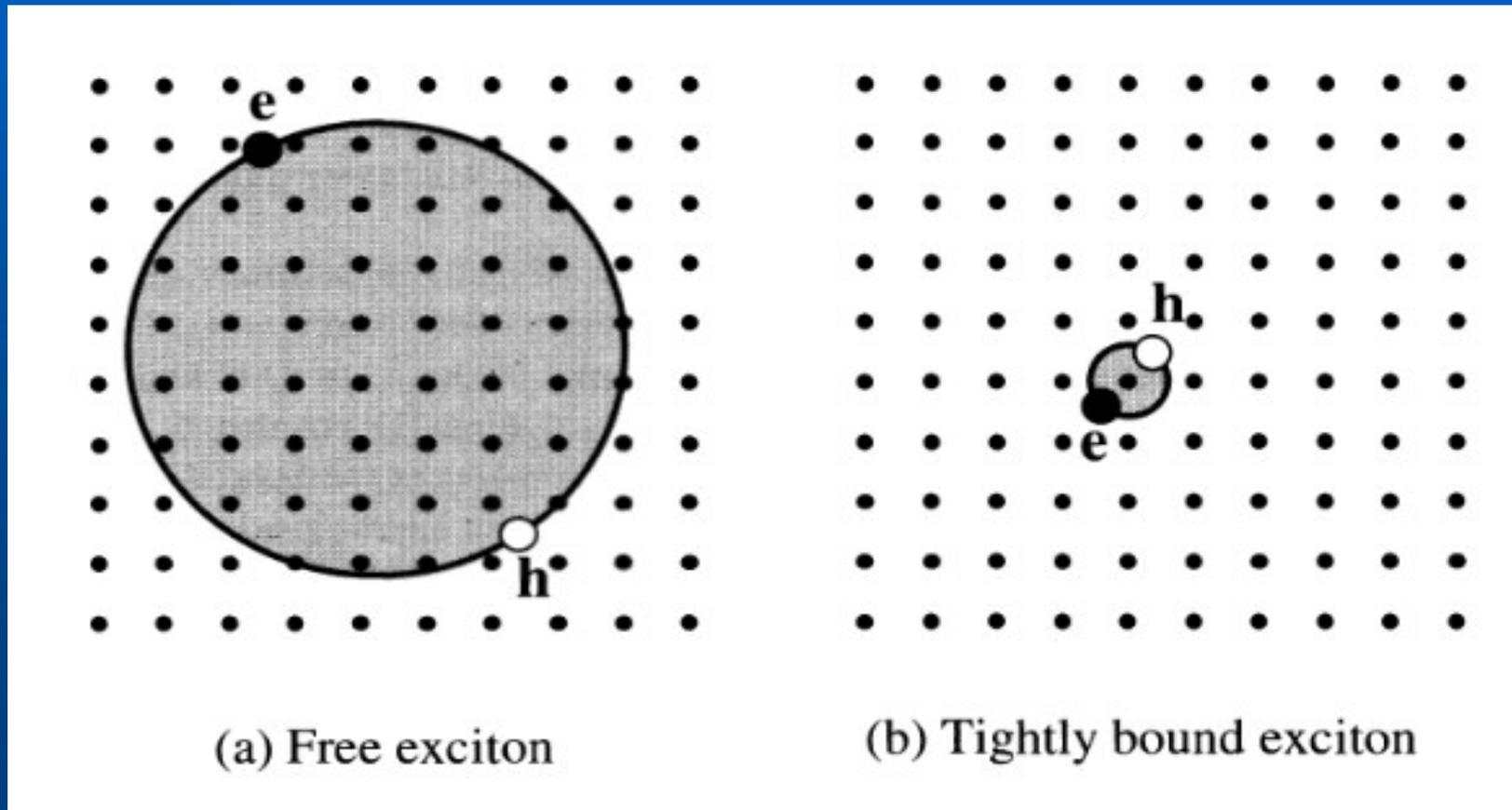


# Impureza Hidrogenoide: Éxciton Localizado



Energía de Ligación  $E_L$   $\ll$  Energía del Gap  $E_G$   
 En otro caso  $\Rightarrow$  Deep Level  
 Constante de red  $a_B$  Deformation Crystal  
 Radio de Bohr de la Impureza  $a_B$  Cálculos Pesados (Comp.)

# Éxcitones libres: pares electrón hueco ligados



**Wannier-Mott**

**Frenkel**

# Impureza Hidrogenoide

$$-\frac{\hbar^2}{2m_0} \nabla^2 \Psi(\vec{\mathbf{r}}) + V(\vec{\mathbf{r}}) \Psi(\vec{\mathbf{r}}) = E \Psi(\vec{\mathbf{r}})$$

Aproximación Masa Efectiva:

$$-\frac{\hbar^2}{2m_e} \nabla^2 F(\vec{\mathbf{R}}) + \Delta V F(\vec{\mathbf{R}}) = \Delta E F(\vec{\mathbf{R}})$$

Masa Efectiva  
del Electron

Función

“Envelope”

# Impureza Hidrogenoide

$$-\frac{\hbar^2}{2m_0} \nabla^2 \Psi(\vec{\mathbf{r}}) + V(\vec{\mathbf{r}}) \Psi(\vec{\mathbf{r}}) = E \Psi(\vec{\mathbf{r}})$$

**Aproximación Masa Efectiva:**

$$-\frac{\hbar^2}{2m_e} \nabla^2 F(\vec{\mathbf{R}}) + \Delta V F(\vec{\mathbf{R}}) = \Delta E F(\vec{\mathbf{R}})$$

**Potencial Impureza**

**Estados de Energía**

**(Apartamiento de Estructura de Bandas)**

# Potencial de Impureza

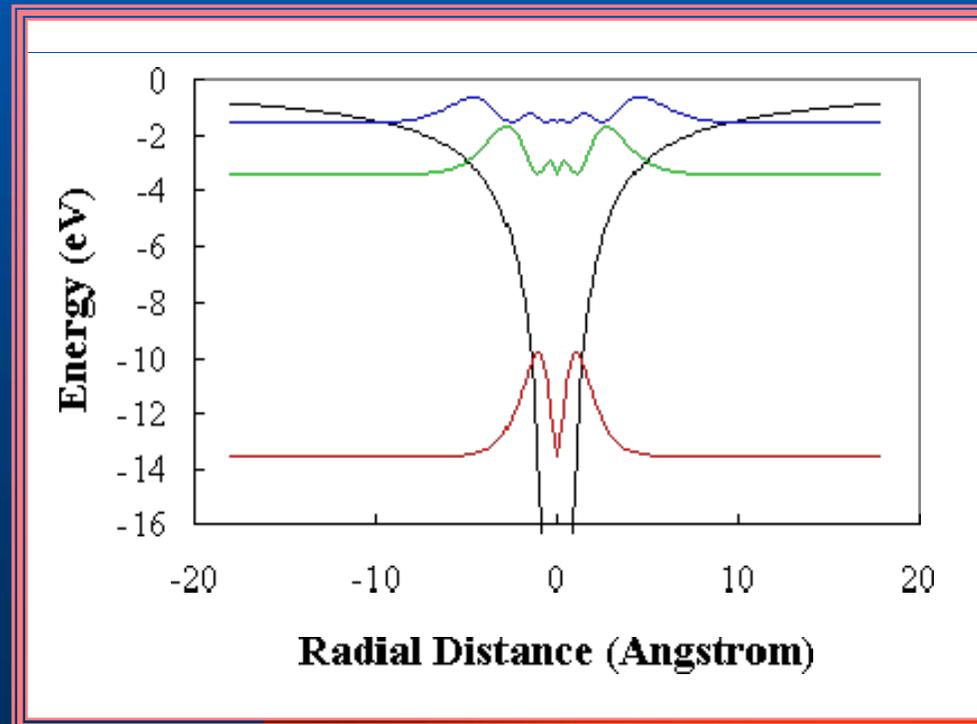
- Interacción de **Coulomb** :  
(Potencial Hidrogenoide)

$$\Delta V(r) = -\frac{1}{4\pi\epsilon\epsilon_0} \frac{e^2}{r}$$

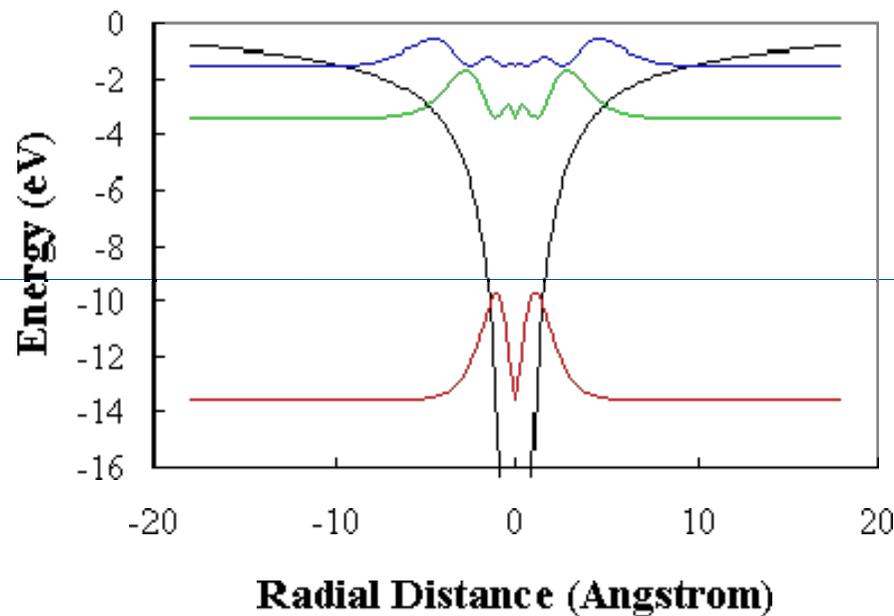
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# Átomo de Hidrógeno



$$E = E_n = -\frac{1}{2} \frac{m^* q^4}{(4\pi\epsilon_0)^2 \hbar^2 n^2}$$

• Radio de Bohr:

$$a_B = \frac{4\pi\epsilon_0 \hbar^2}{m^* q^2}$$

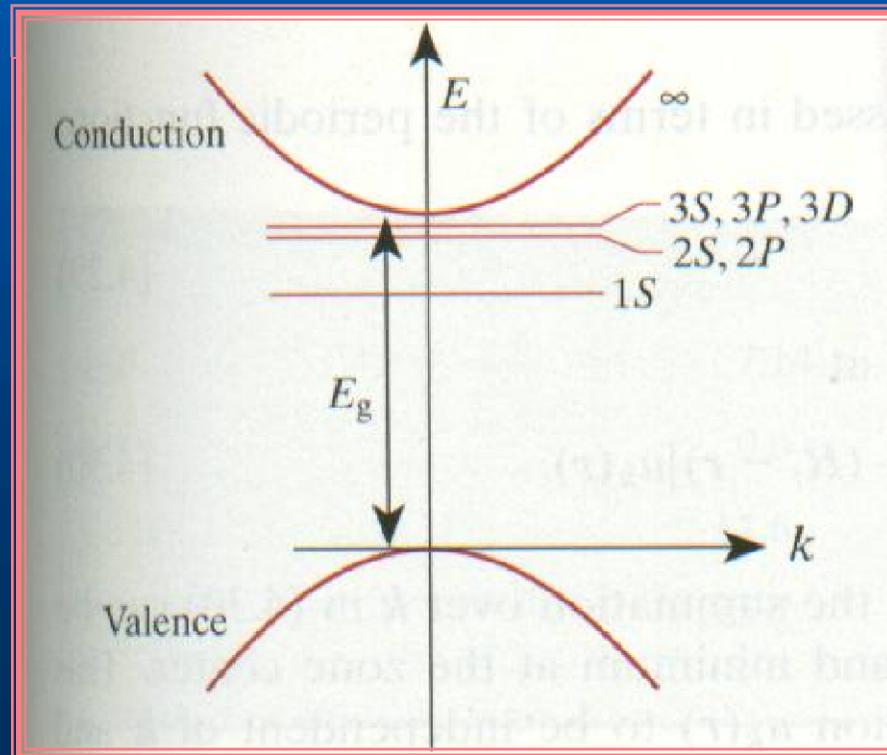
$$E_n = -\left(\frac{q^2}{4\pi\epsilon_0}\right)^2 \frac{m^*}{2\hbar^2} \frac{1}{n^2} = -\frac{\hbar^2}{2m^* a_B^2} \frac{1}{n^2} = -\frac{1}{2} \frac{q^2}{4\pi\epsilon_0 a_B} \frac{1}{n^2} = -\frac{\mathfrak{R}}{n^2}$$

$\mathfrak{R} \rightarrow$  Energía de Rydberg = 13.6 eV

# Potencial de Impureza

- Interacción de **Coulomb** :  
(Potencial Hidrogenoide)

$$\Delta V(r) = -\frac{1}{4\pi\epsilon\epsilon_0} \frac{e^2}{r}$$



# Potencial de Impureza

- Interacción de **Coulomb** :  
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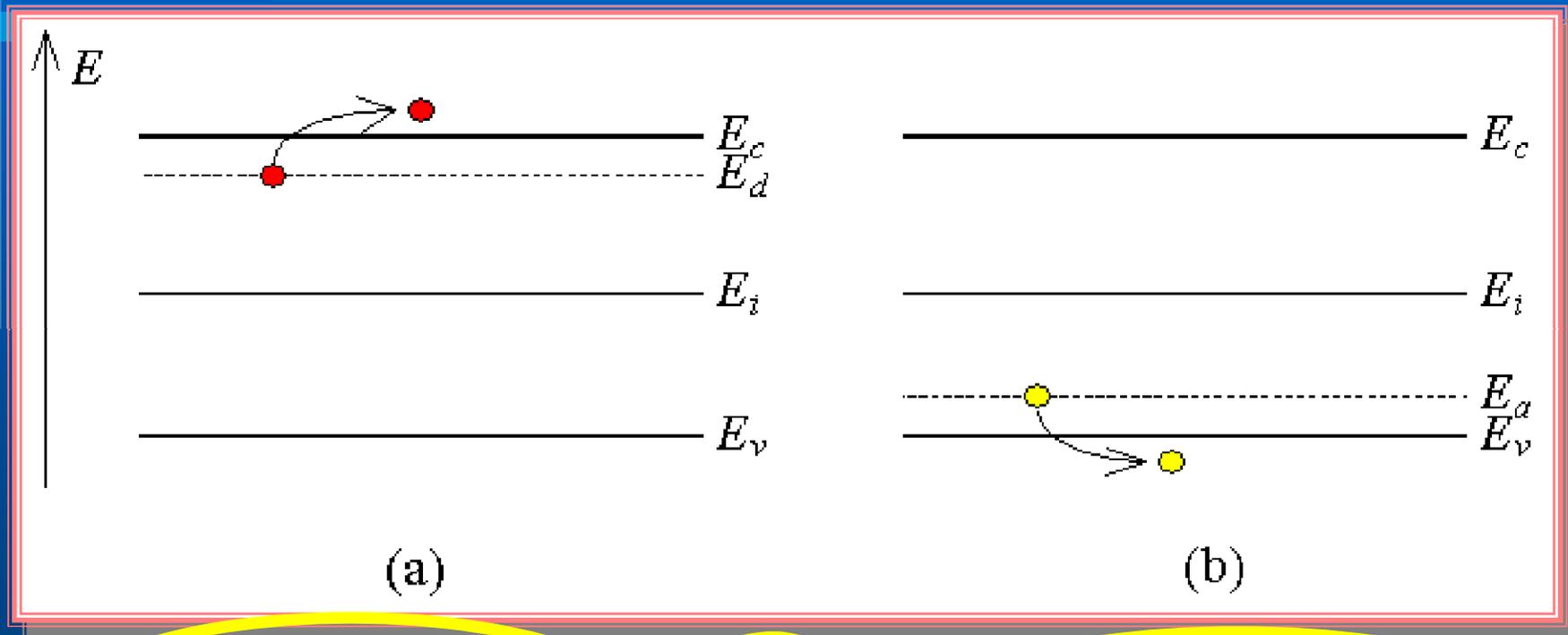
- **Binding Energy**  
(Energía de Ligación):  
( $R_H = 13.6 \text{ eV}$ )

$$\Delta E = -\left(\frac{m_e}{m_0}\right)\left(\frac{1}{\epsilon^2}\right)R_H$$

- **Radio de Bohr**  
de la Impureza:  
( $a_H = 0.53 \text{ \AA}$ )

$$a_B = \epsilon \left(\frac{m_0}{m_e}\right) a_H$$

# Shallows: “Dadores” vs. “Aceptores”

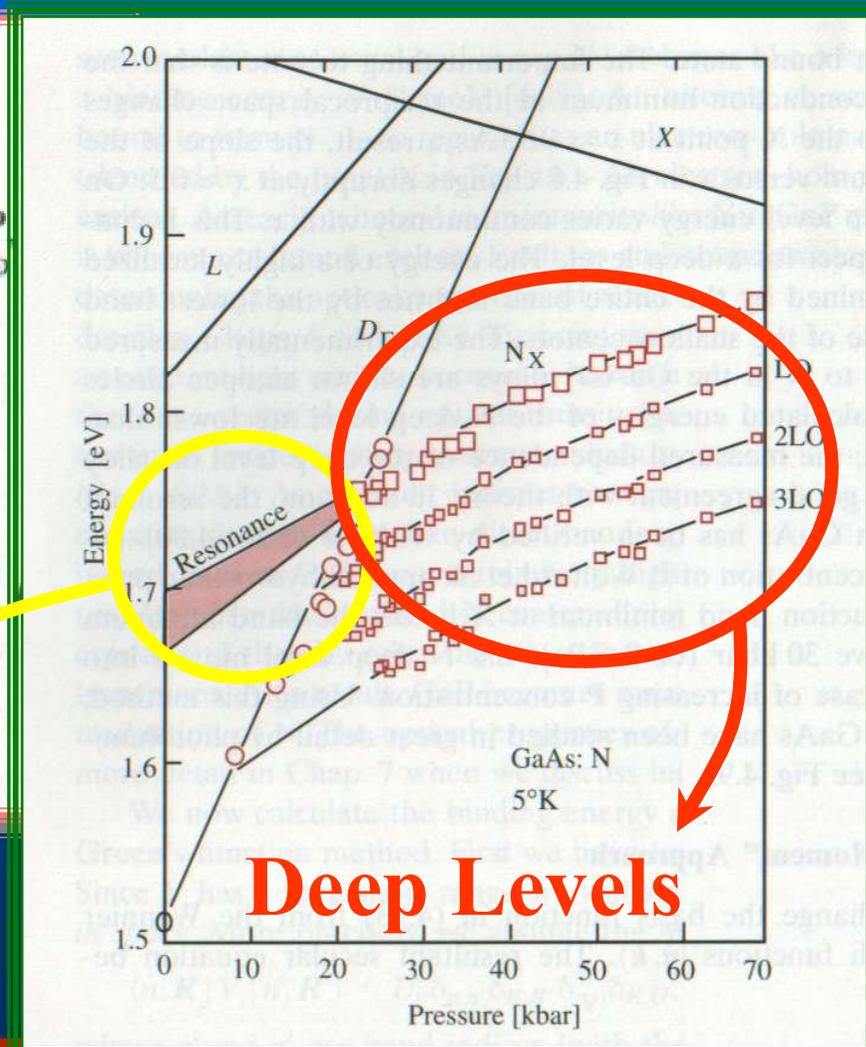
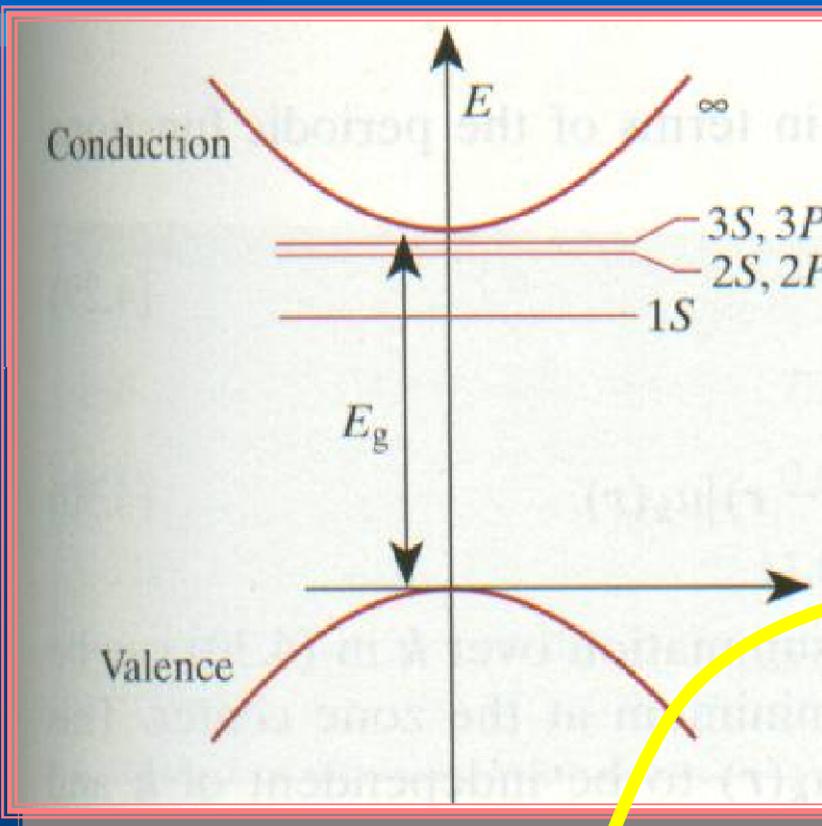


• “Dador”  $\Rightarrow n$ -type

• “Aceptor”  $\Rightarrow p$ -type

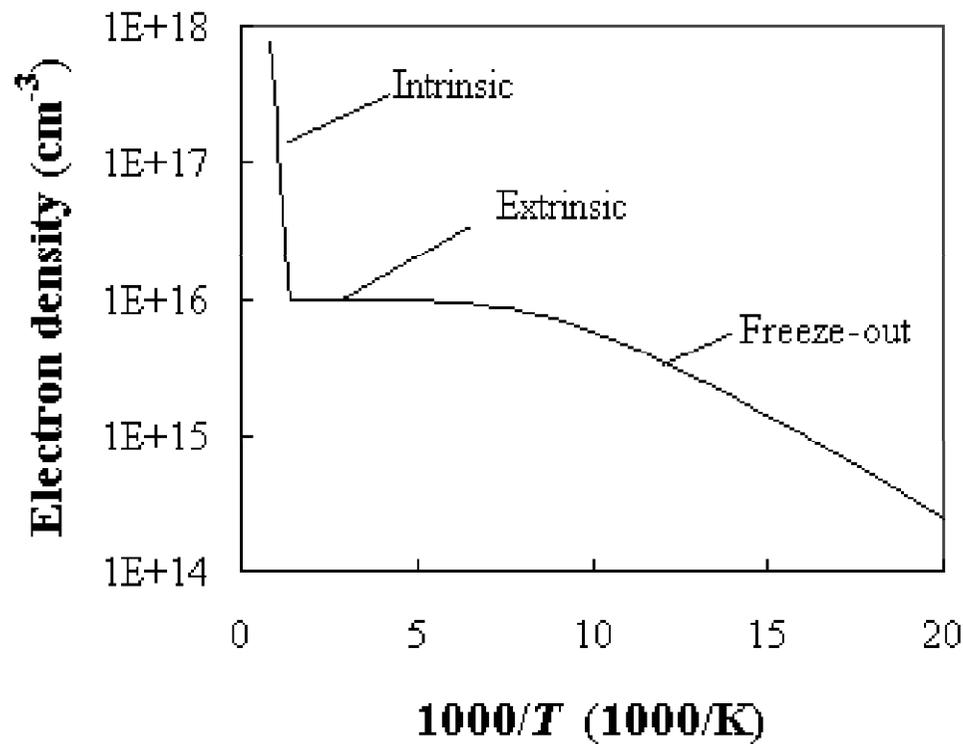
• Balance da lugar a “Autocompensación”

# “Shallow” vs “Deep”



Estados Resonantes

# Efecto del Dopaje



$$\mu = \frac{e\tau}{m_e}$$

$$\rho = \frac{m_e}{ne^2\tau}$$

# Potencial de Impureza

- Interacción de **Coulomb** :  
(Potencial Hidrogenoide)

$$\Delta V(r) = -\frac{1}{4\pi\epsilon\epsilon_0} \frac{e^2}{r}$$

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de la Impureza:  
( $a_H = 0.53 \text{ \AA}$ )

$$a_B = \epsilon \left(\frac{m_0}{m_e}\right) a_H$$

# Excitones

$$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_h}$$

- Interacción de **Coulomb** :  
(Potencial Hidrogenoide)

$$\Delta V(r) = -\frac{1}{4\pi\epsilon\epsilon_0} \frac{e^2}{r}$$

- Binding Energy  
(Energía de Ligación):  
( $R_H = 13.6 \text{ eV}$ )

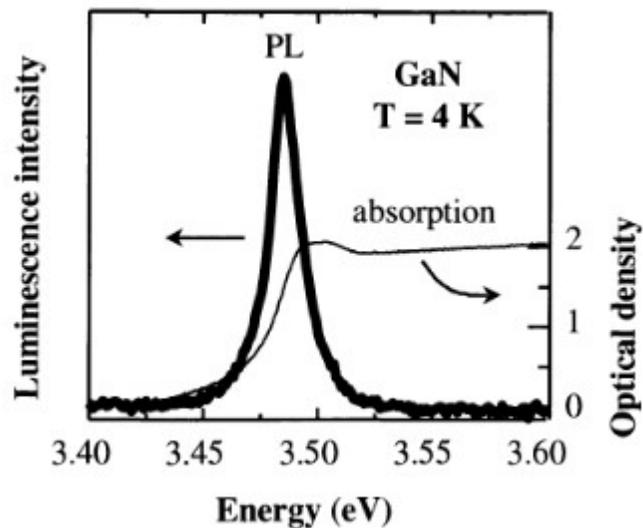
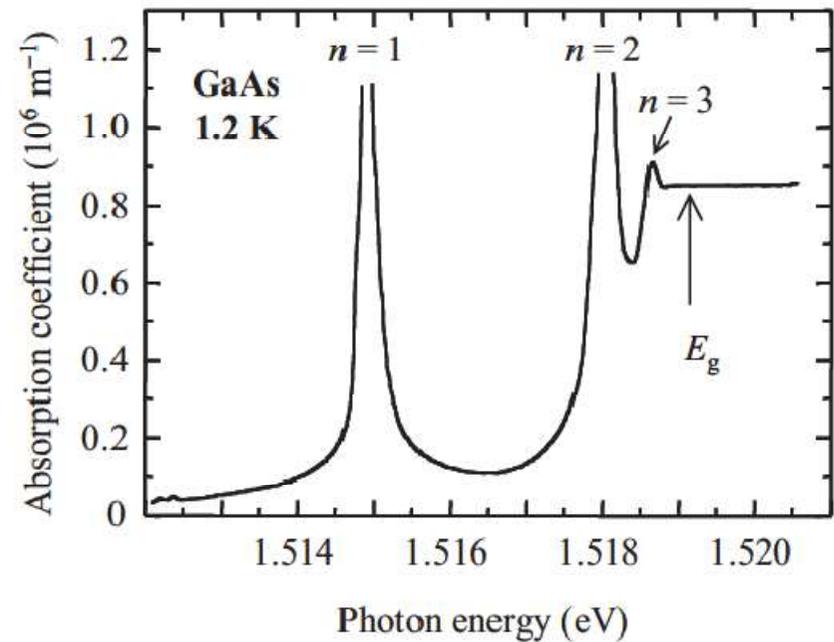
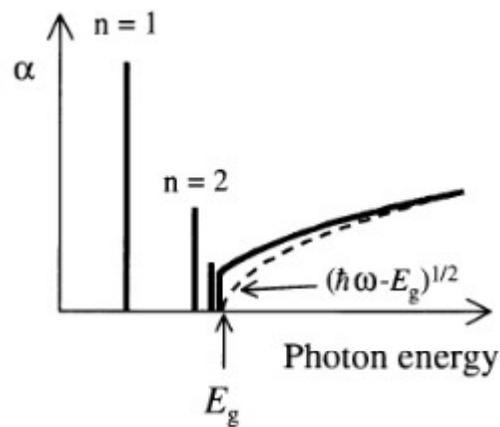
$$\Delta E = -\left(\frac{\mu}{m_0}\right)\left(\frac{1}{\epsilon^2}\right)R_H$$

- Radio de Bohr  
del Excitón:

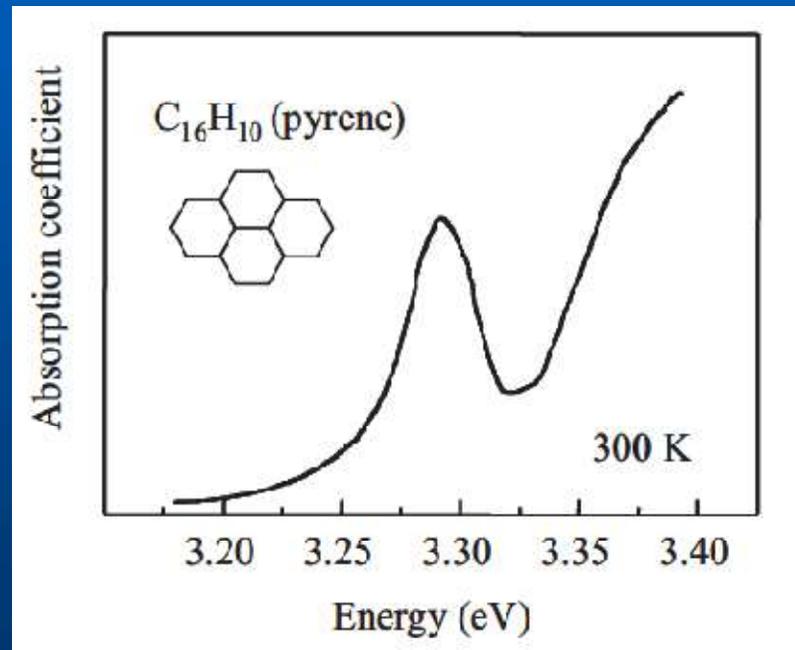
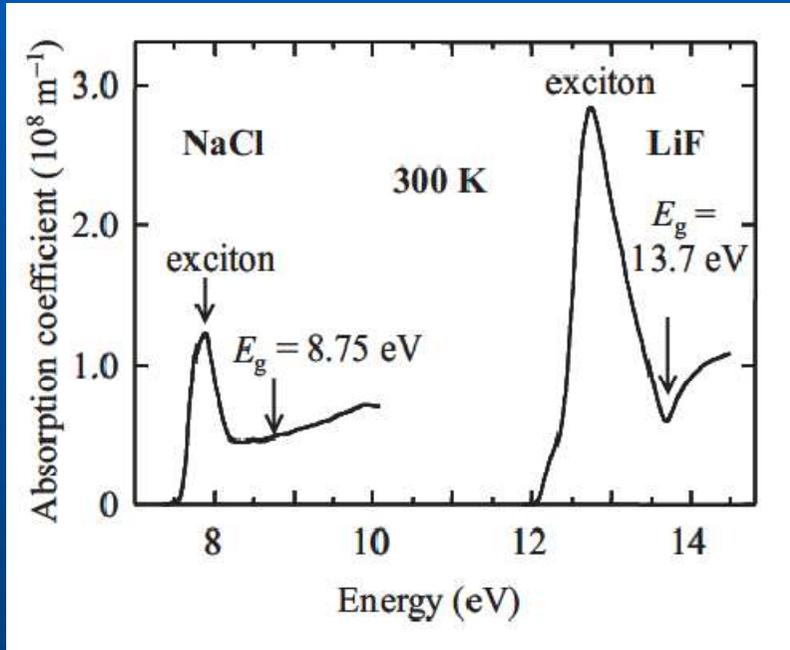
$$a_B = \epsilon \left(\frac{m_0}{\mu}\right) a_H$$

$$(a_H = 0.53 \text{ \AA})$$

# Propiedades Ópticas de Excitones

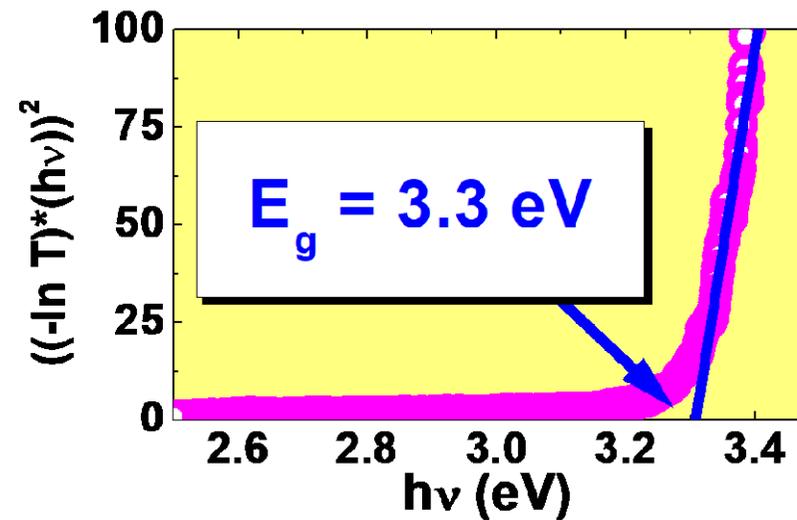
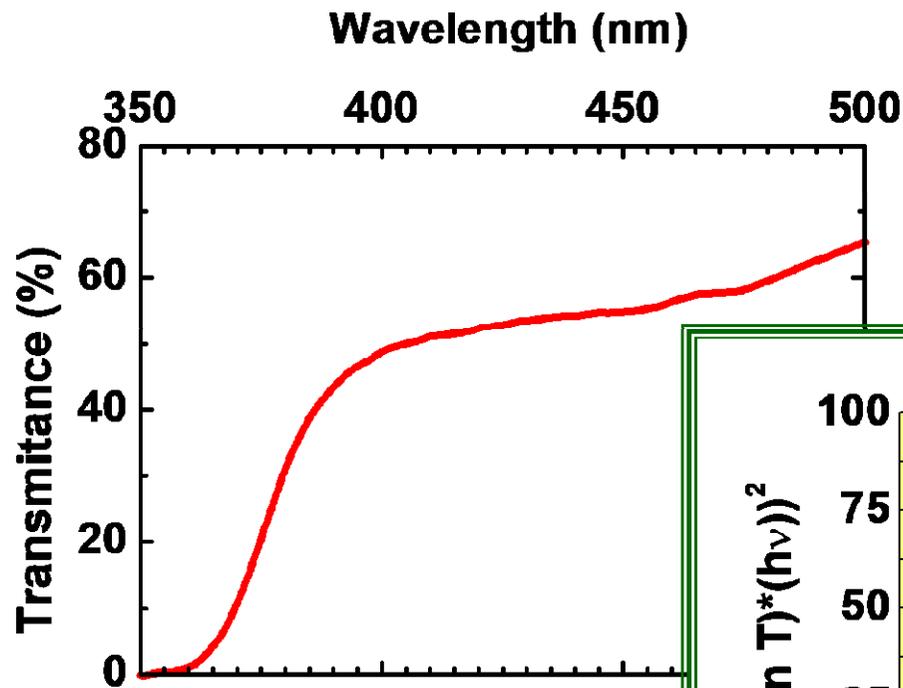


# Excitones de Frenkel



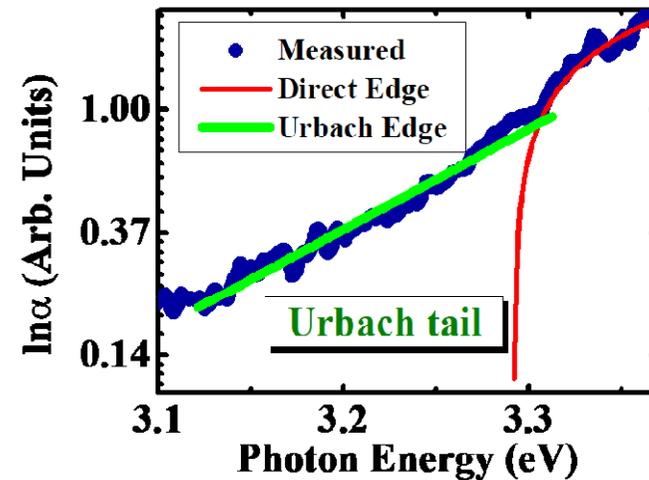
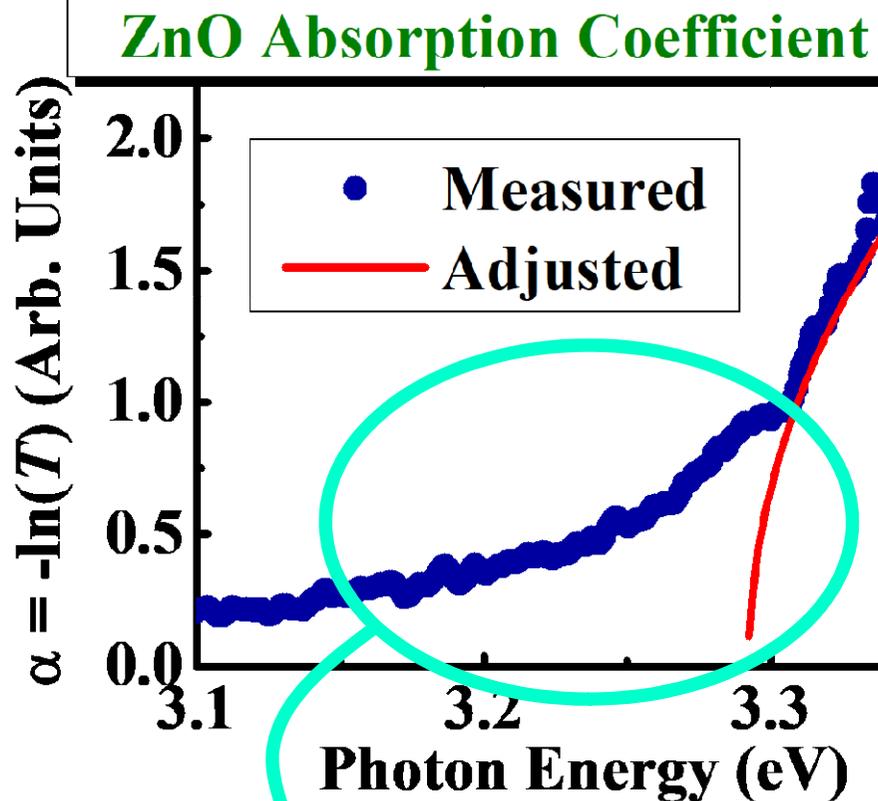
# ZnO

ZnO depositado electroquímicamente en vidrios con ITO (Indium “Tin” Oxide).



*Solar Energy Materials and Solar Cells, 70, 245 – 254 (2001).*

# “Band Tailing”

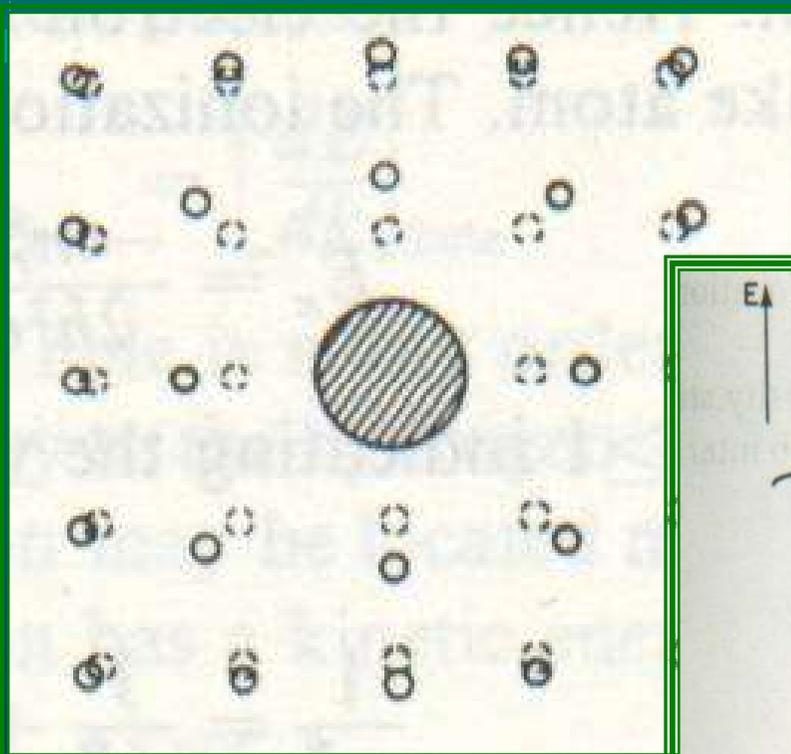


$$\alpha \propto \exp\left(\frac{h\nu}{E_d}\right)$$

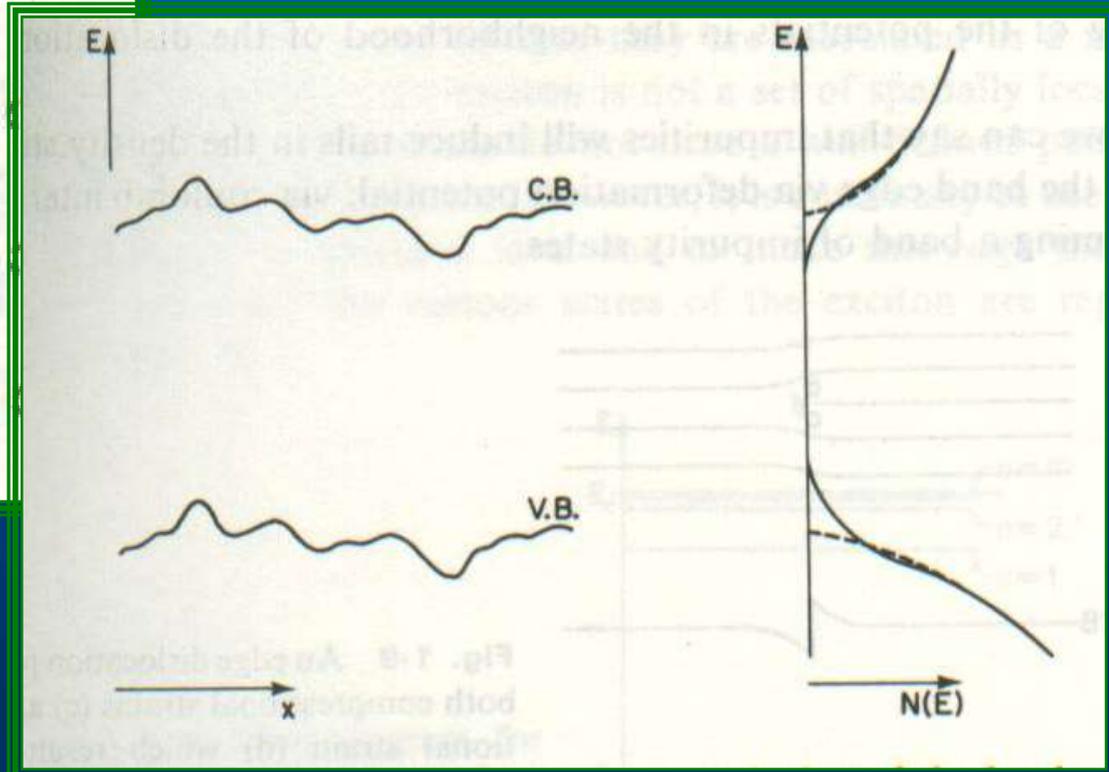
**Below Gap Absorption**

# Band Tailing

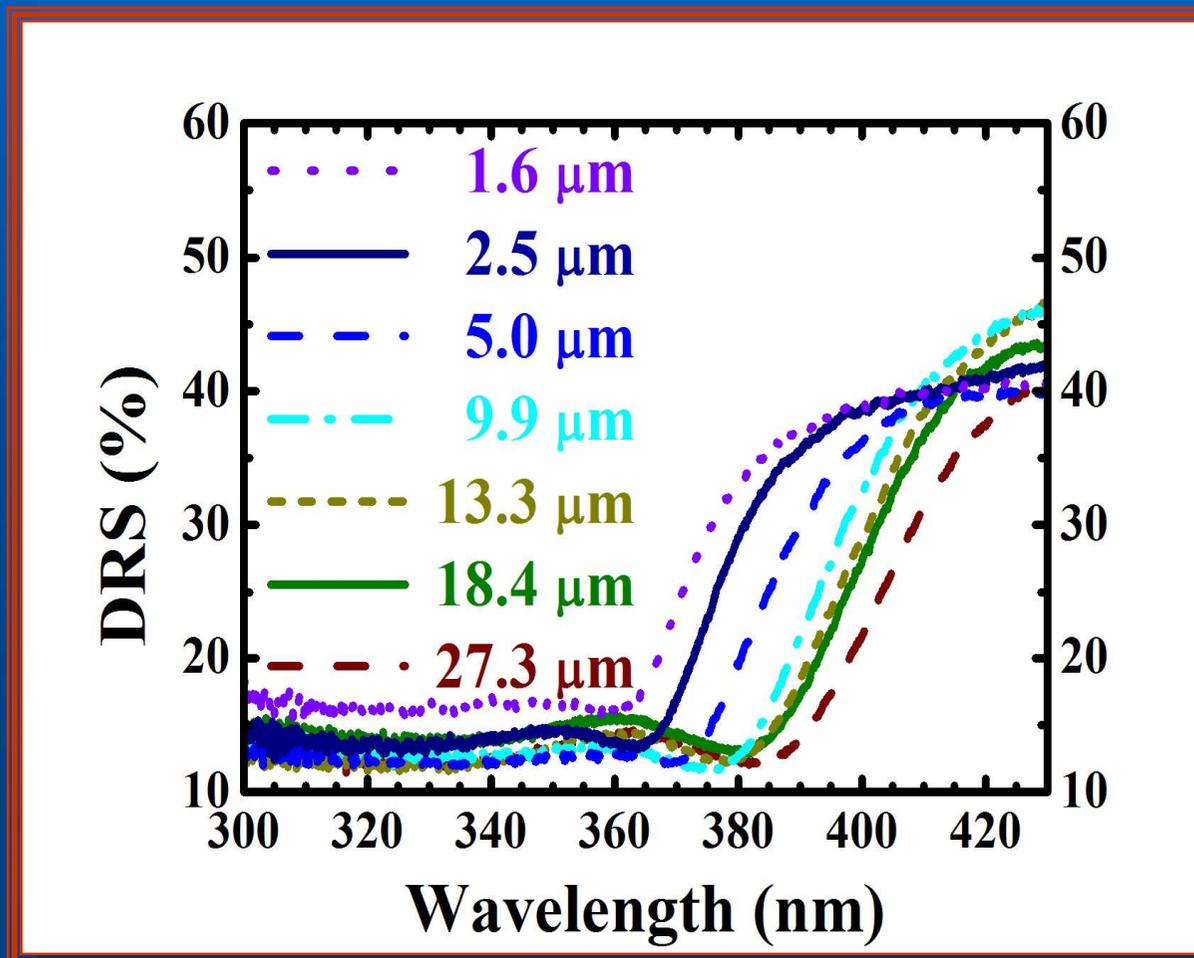
J. I. Pankove, *Optical Processes in Semiconductors*



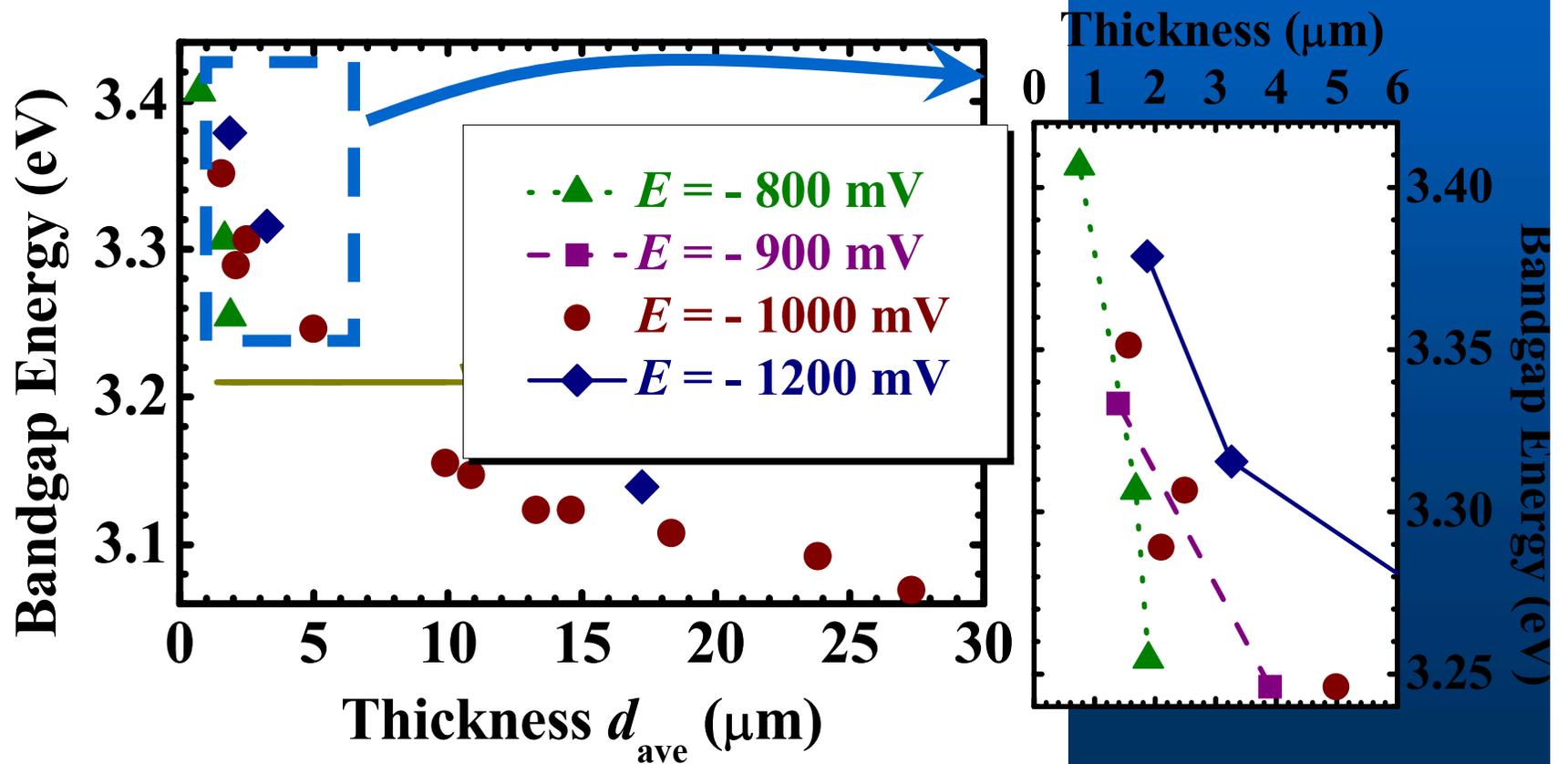
Urbach's Tail  
(1953)



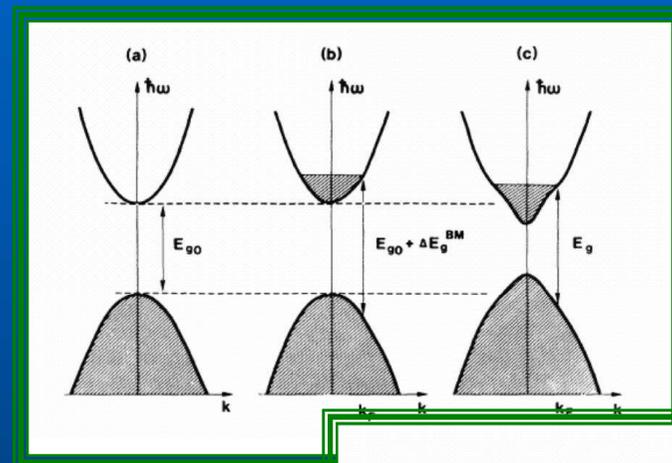
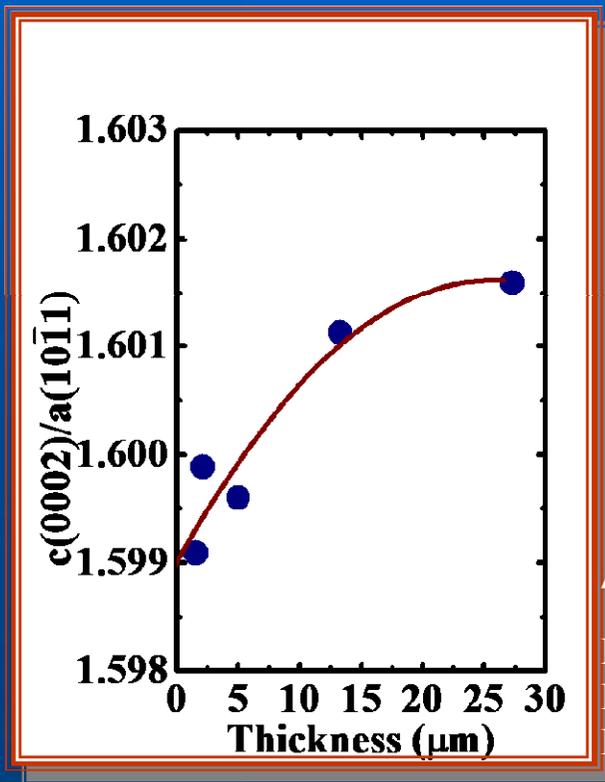
# Reflectancia contra Espesor $d$



# Borde de Absorción contra Espesor

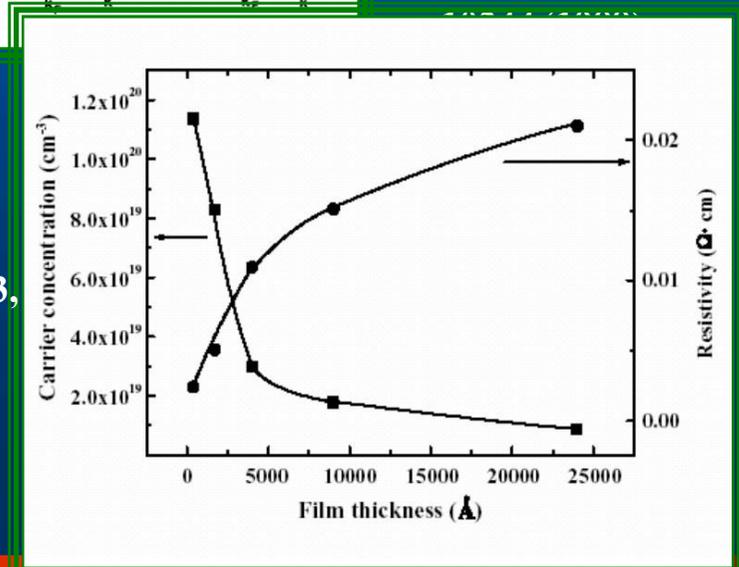


# Efecto Moss-Burstein



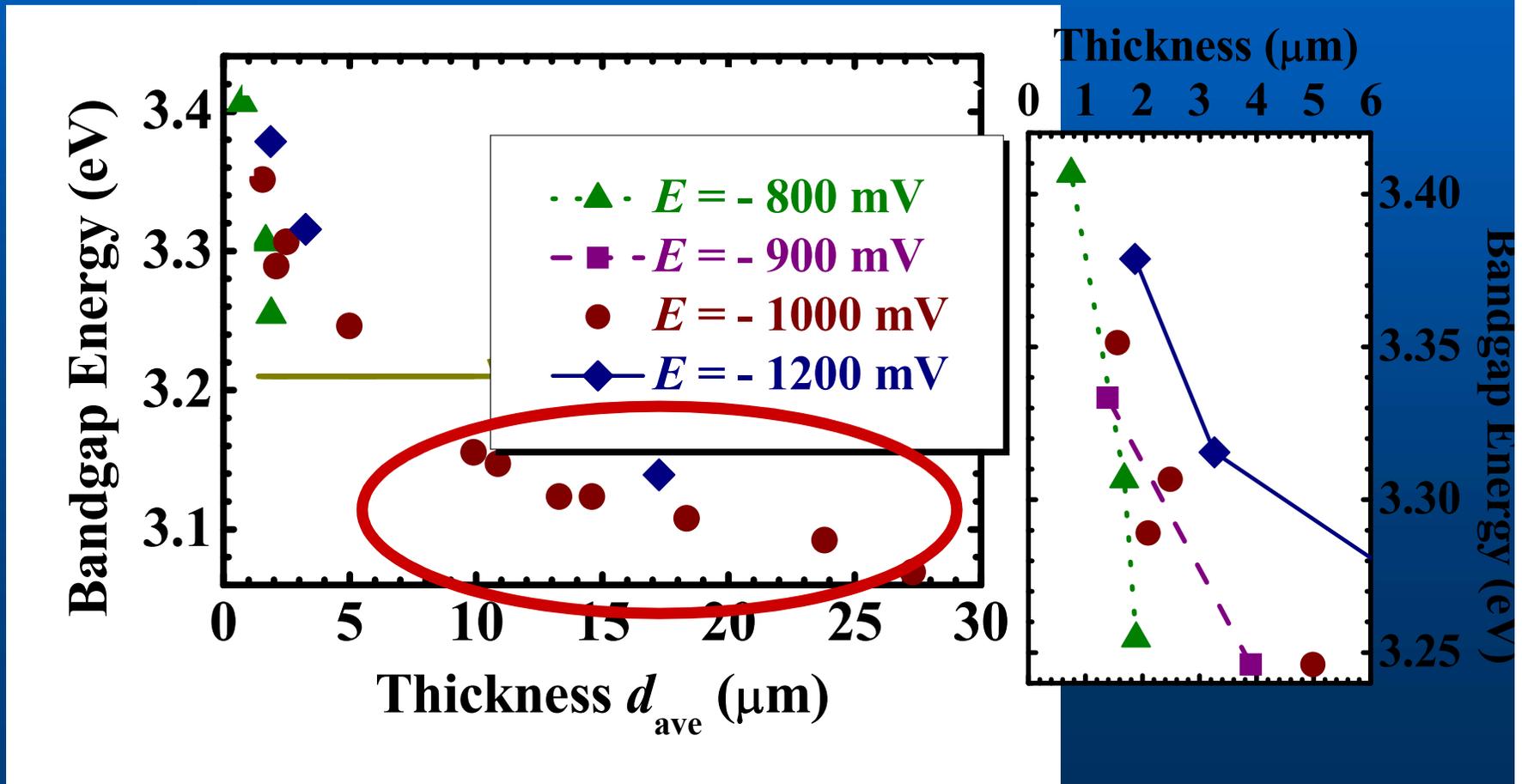
- Heavily doped *n*-type ZnO:  
B. E. Sernelius,  
Phys. Rev. B 37 (17),

$\Delta(c/a)$ : Zn<sub>i</sub>  
M. Izaki, T. Omi, J.  
Electrochem. Soc. 143,  
L53 (1996).

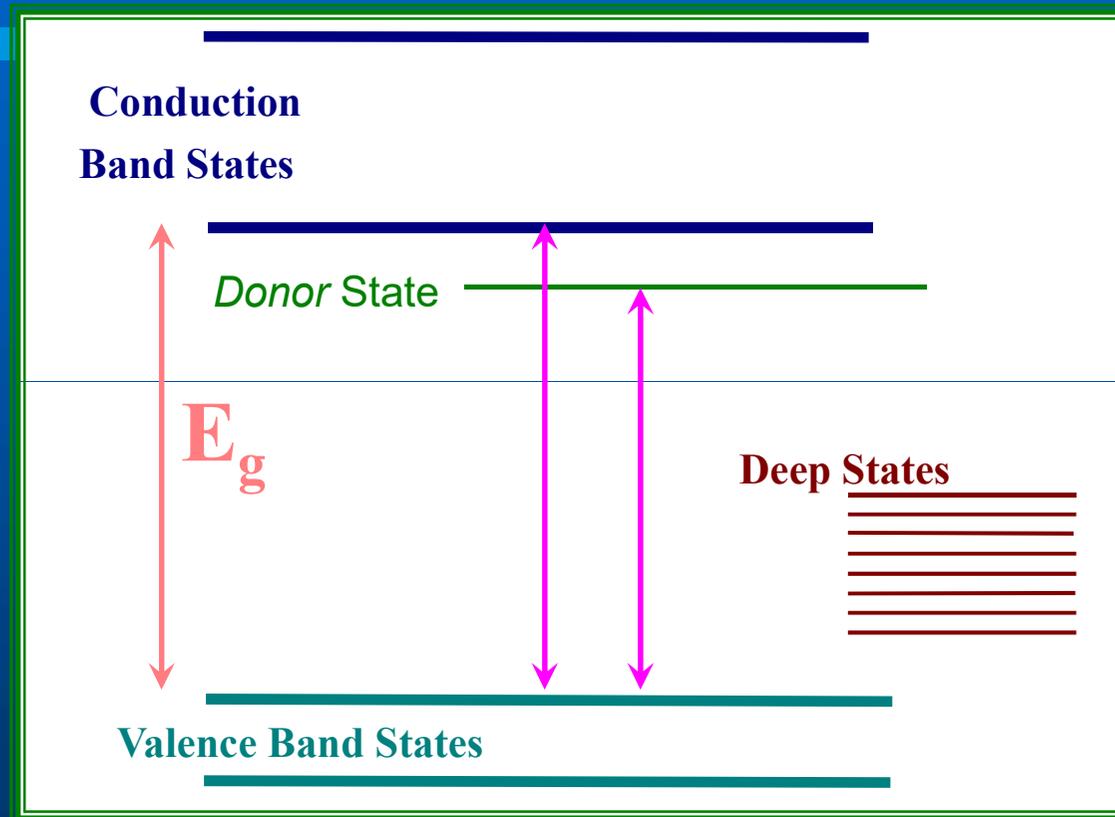


- Auto “doping”:  
J. M. Myoung, Jpn. J. Appl. Phys. 41, 28 (2002).

# Borde de Absorción contra Espesor



# Band-Donor Absorption



- **ZnO:** V. Srikant and D. R. Clarke, *J. Appl. Phys.* 83 (10), 5447 (1998).

# Propiedades Ópticas de Semiconductores

- Estructura Electrónica
- Absorción Óptica en Semiconductores
- **Influencia de Defectos**
- **Excitones**
- Efectos Nanométricos

# Propiedades Ópticas de Semiconductores

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# Reducción Dimensionalidad en Semiconductores

## ➤ QW (“Quantum Wells”)

- Confinamiento 1D.
- Sistemas 2D.

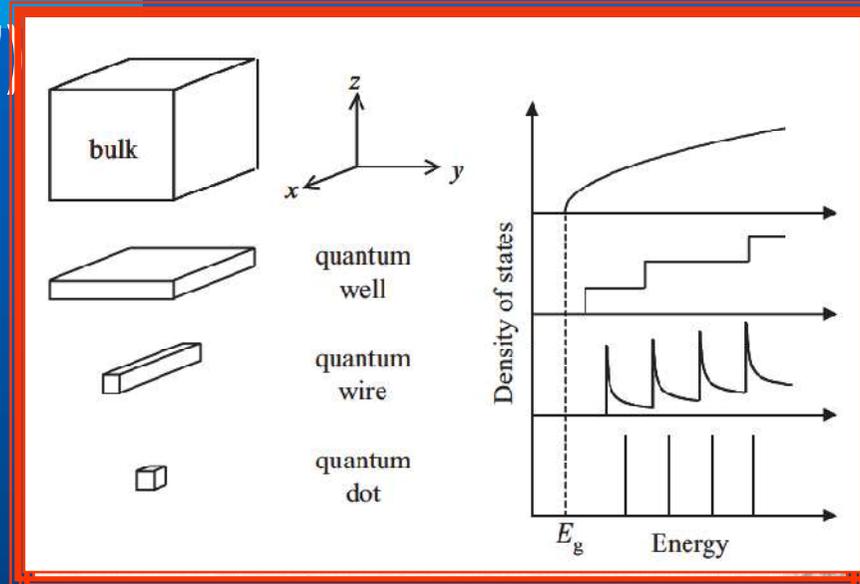
## ➤ Qw (“Quantum Wires”)

### o Hilos Cuánticos):

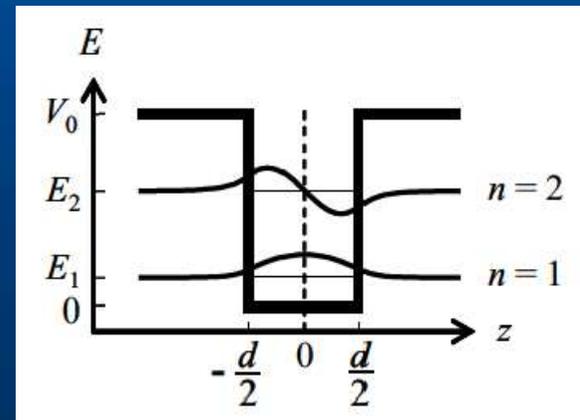
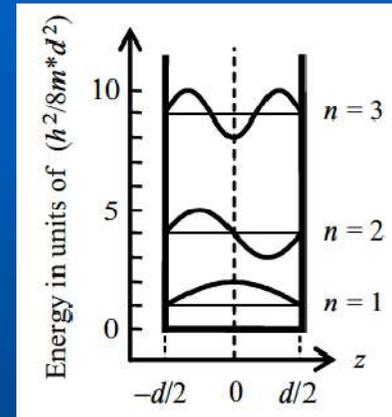
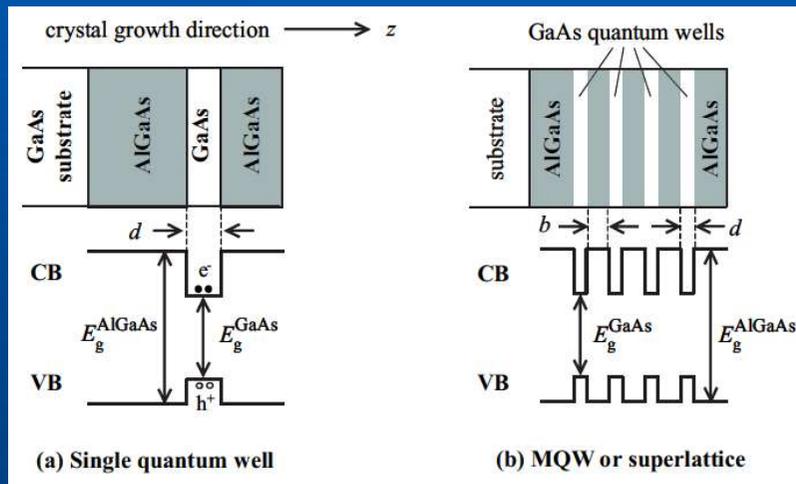
- Confinamiento 2D.
- Sistemas 1D.

## ➤ QD (“Quantum Dots” & “Quantum Boxes” = Puntos Cuánticos y Cajas Cuánticas):

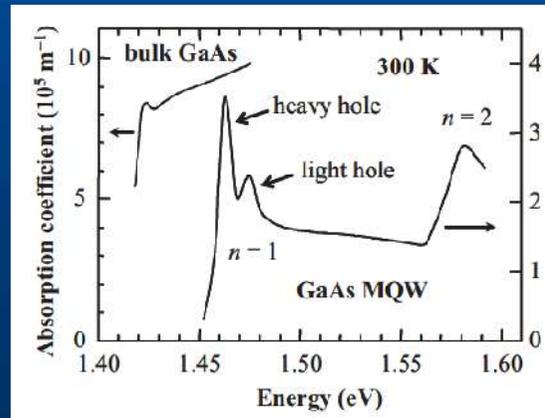
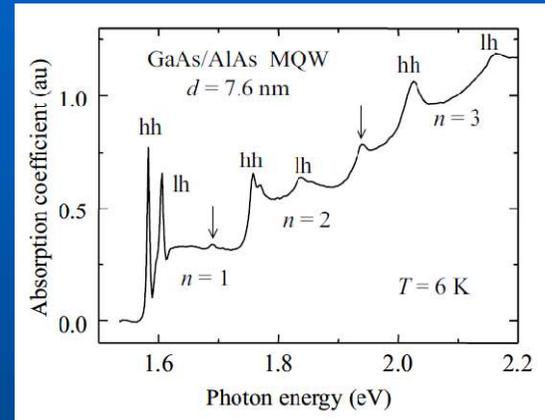
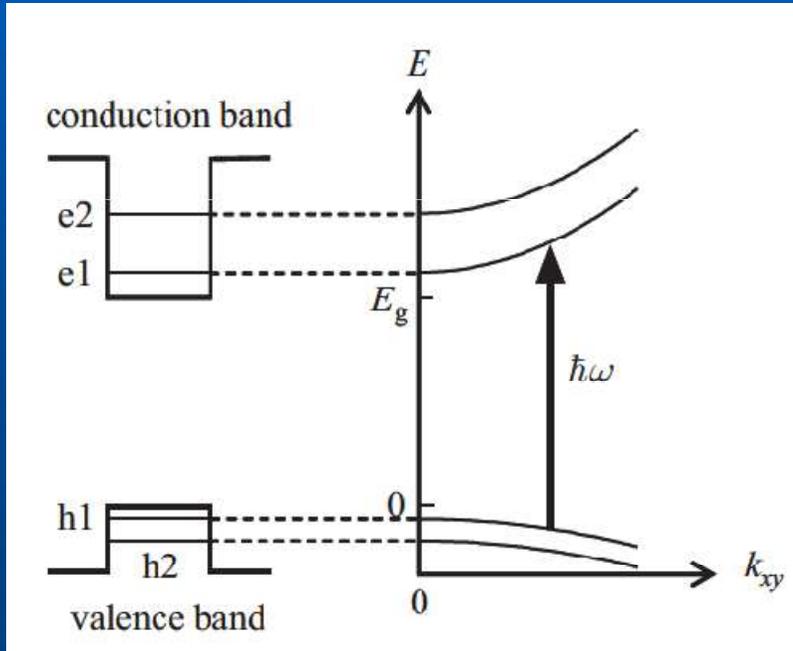
- Confinamiento 3D.
- Sistemas 0D.



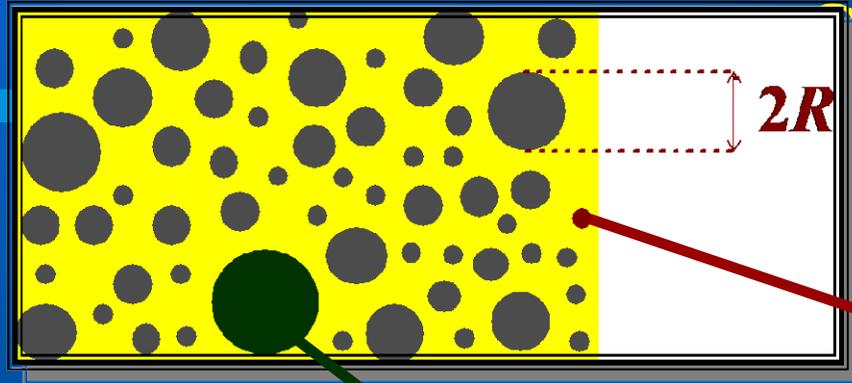
# Quantum Wells



# Quantum Wells



# Puntos Cuánticos semiconductores



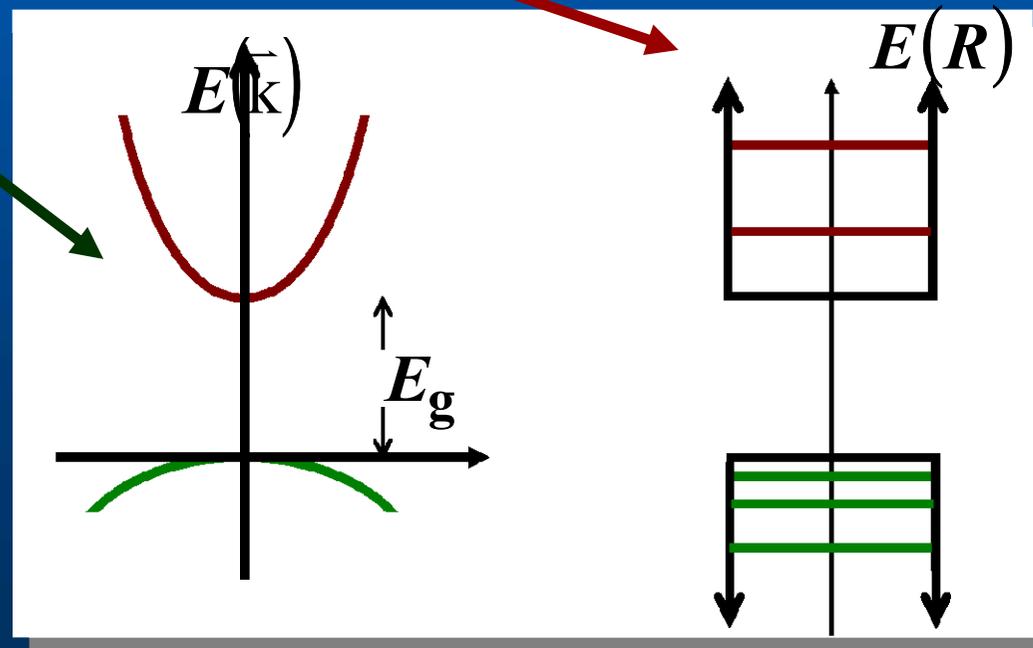
- Semiconductor.
- Vidro

$$R \sim a_{exc}, R < a_{exc}$$

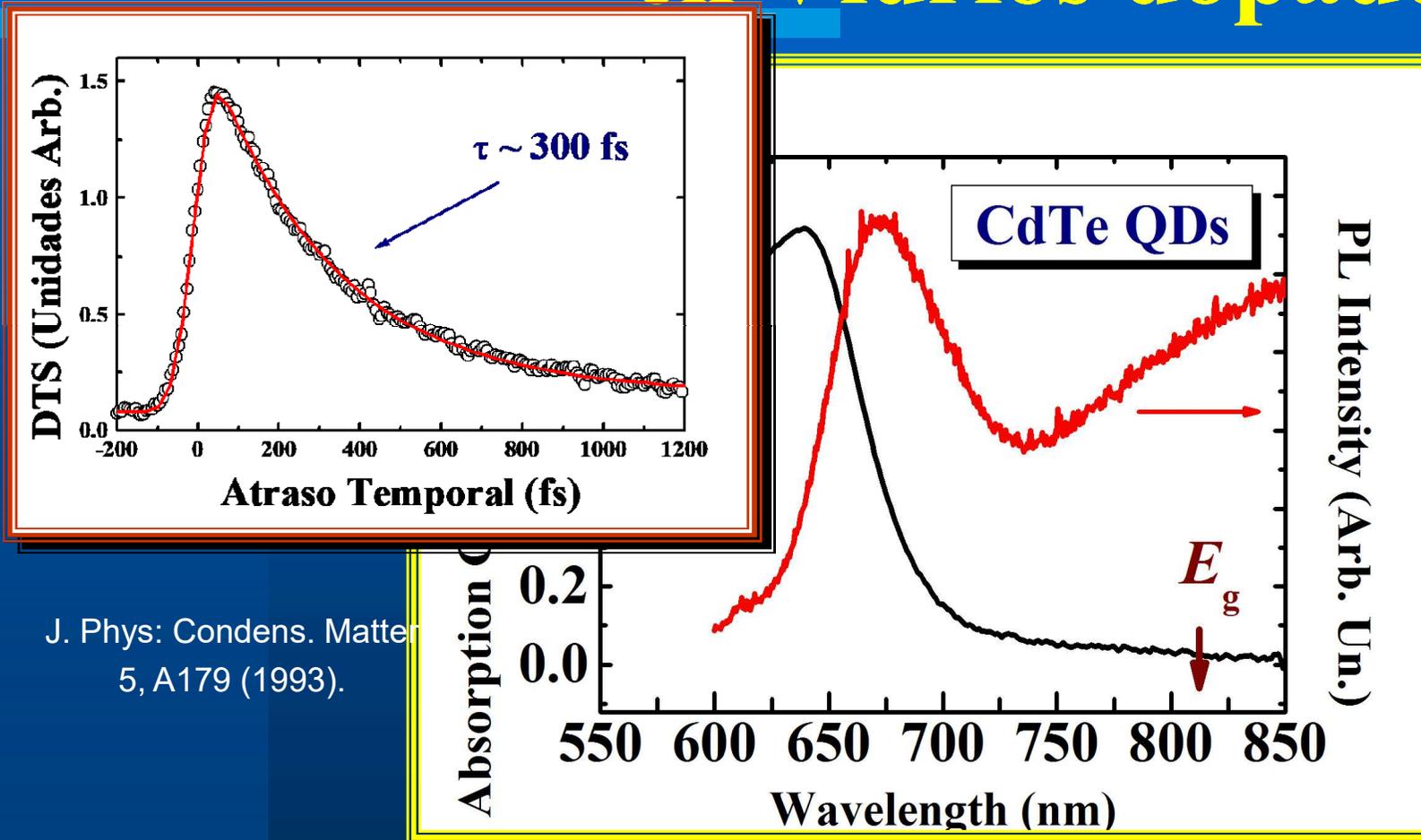
$$R \gg a_{exc}$$

Para CdTe:

$$a_{exc} = 75 \text{ \AA}$$



# Absorción y Emisión de Luz en Vidrios dopados

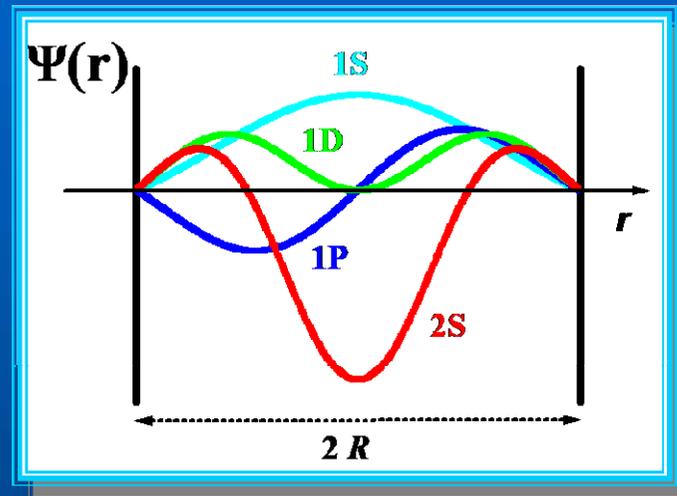
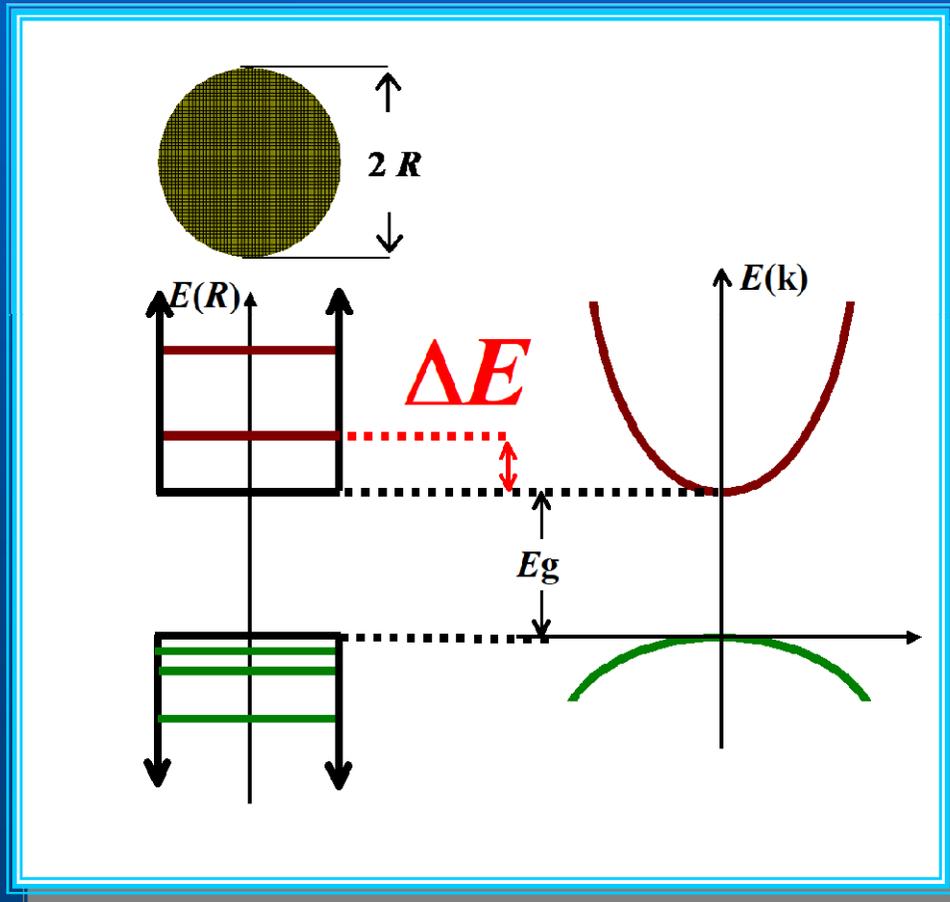


J. Phys: Condens. Matter  
5, A179 (1993).

Appl. Phys. Lett. 59, 2715 (1991).

Caracterización Óptica, Ricardo Marotti, khamul@fing.edu.uy, Montevideo, Junio 2015

# Confinamiento Cuántico.

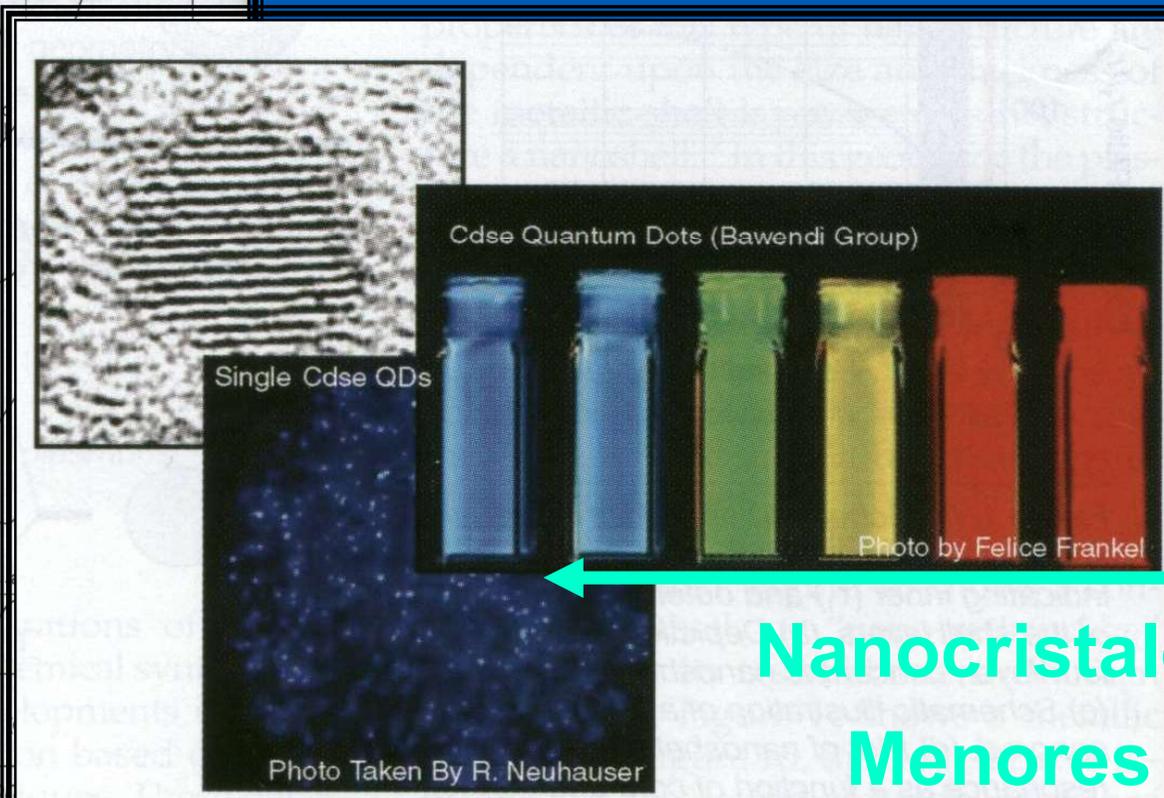
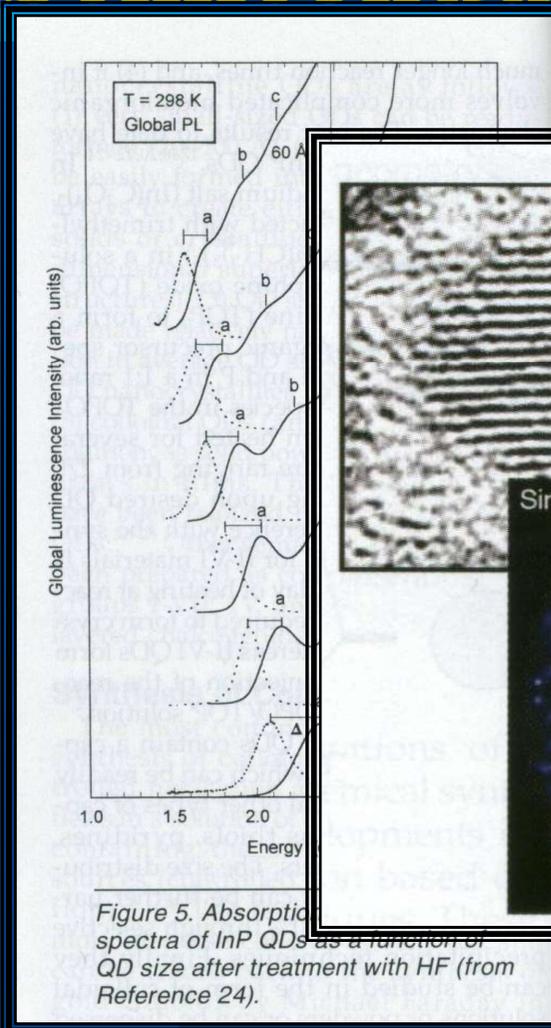


Modelo Simple:

$$\Delta E \propto \frac{1}{R^2}$$

# Puntos Cuánticos Coloidales de Semiconductores III-V y II-VI.

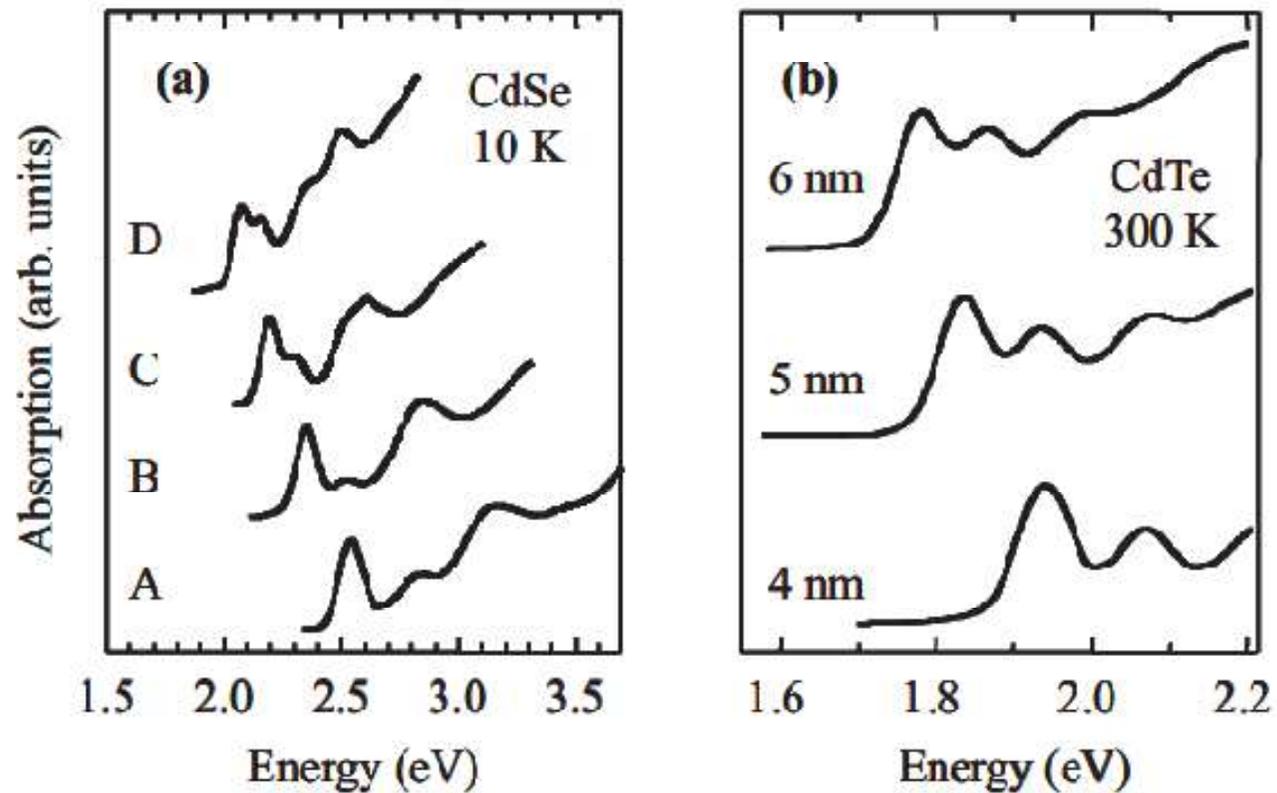
MRS Bulletin 23, 23 (1998)



Nanocristales Menores

MRS Bulletin 30, 362 (2005)

# Puntos Cuánticos Coloidales de Semiconductores II-VI.



# Parámetros Confinamiento Cuántico

$$\Delta E = E(R) - E_g = E_b \left( \frac{\pi a_B}{R} \right)^2$$

- Exciton Binding Energy:  
( $R_H = 13.6 \text{ eV}$ )

$$E_b = - \left( \frac{\mu}{m_0} \right) \left( \frac{1}{\epsilon^2} \right) R_H$$

- Exciton Bohr Radius:  
( $a_H = 0.53 \text{ \AA}$ )

$$a_B = \epsilon \left( \frac{m_0}{\mu} \right) a_H$$

# Parámetros Confinamiento Cuántico

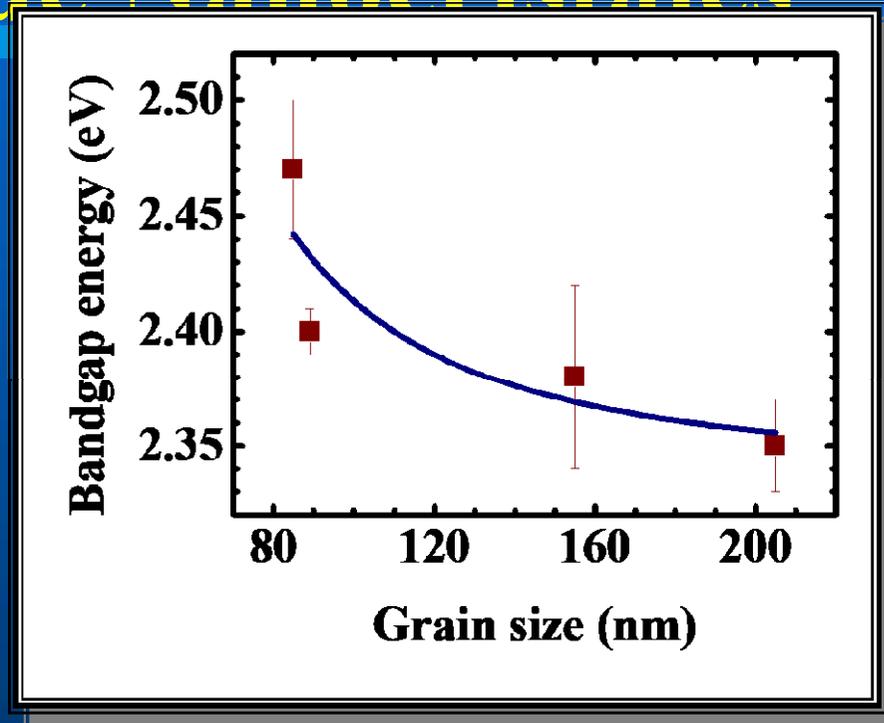
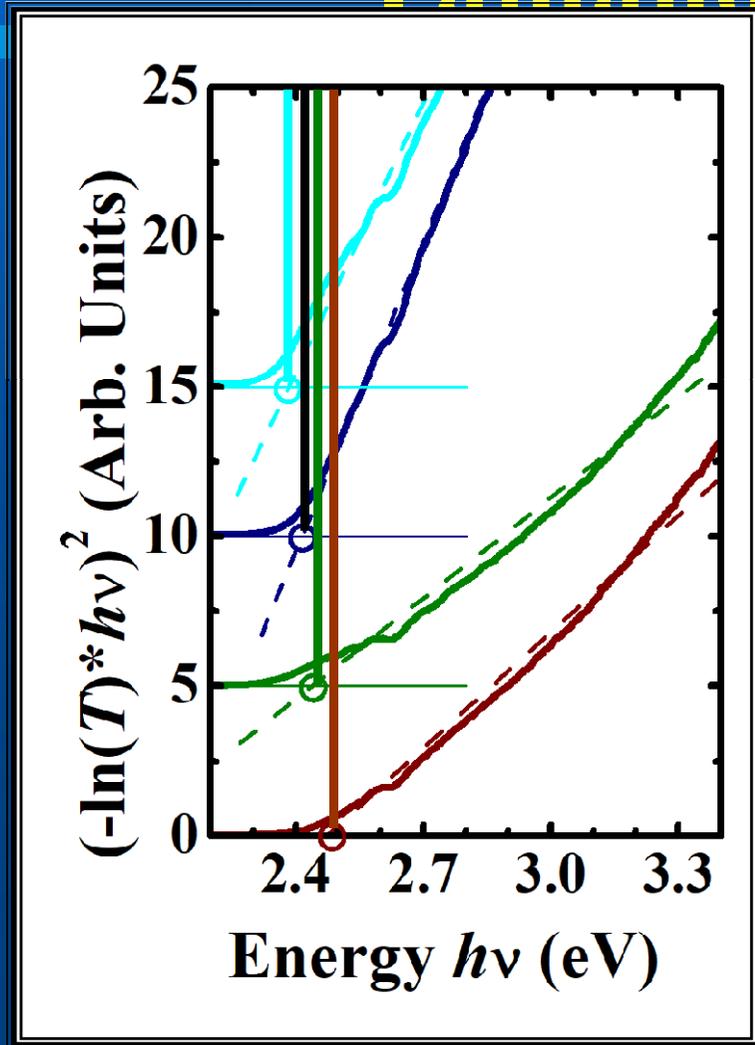
$$\Delta E = E(R) - E_g = E_b \left( \frac{\pi a_B}{R} \right)^2$$

- $E_b$ : "Exciton Binding Energy"
- $a_B$ : "Exciton Bohr Radius"
- CdTe:  $a_B = 75 \text{ \AA}$ ,  $E_b = 10 \text{ meV}$  ( $E_g = 1.49 \text{ eV}$ )
- CdS:  $a_B = 30 \text{ \AA}$ ,  $E_b = 27 \text{ meV}$  ( $E_g = 2.42 \text{ eV}$ )
- ZnO:  $a_B = 20 \text{ \AA}$ ,  $E_b = 60 \text{ meV}$  ( $E_g = 3.30 \text{ eV}$ )

# Semiconductores Nanoestructurados

- CdS
- ZnO

# CdS (cúbico): $E_g$ contra Tamaño de Nanocristales

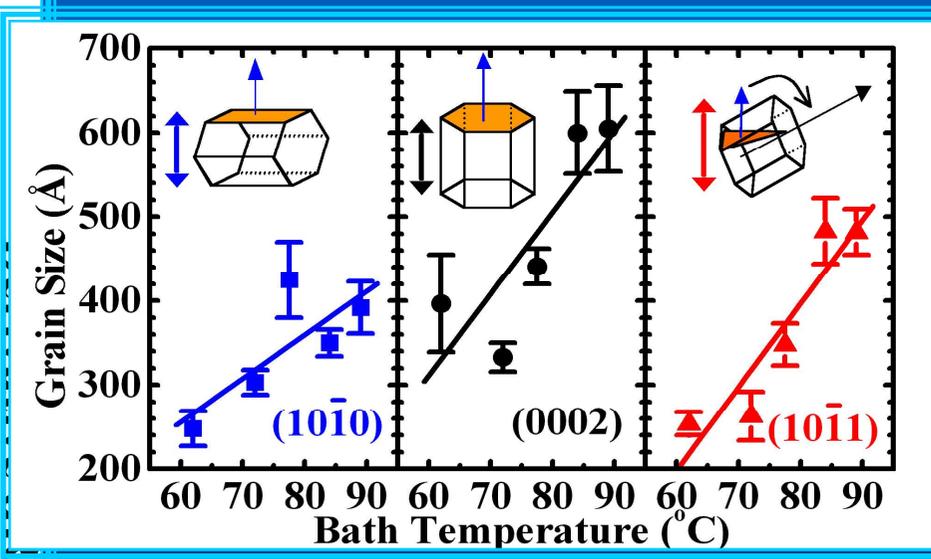
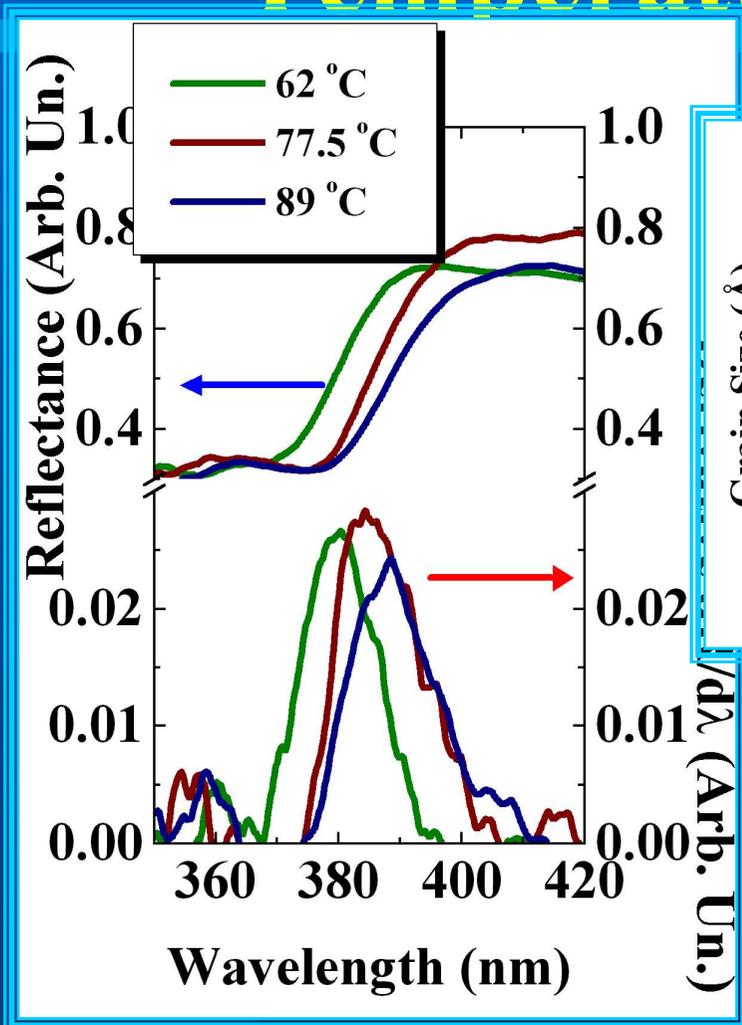


Solar Energy Materials and Solar  
Cells 82, 21 (2004).

$$E_g \propto \frac{1}{D^2} \Rightarrow QC$$

**OK!!**

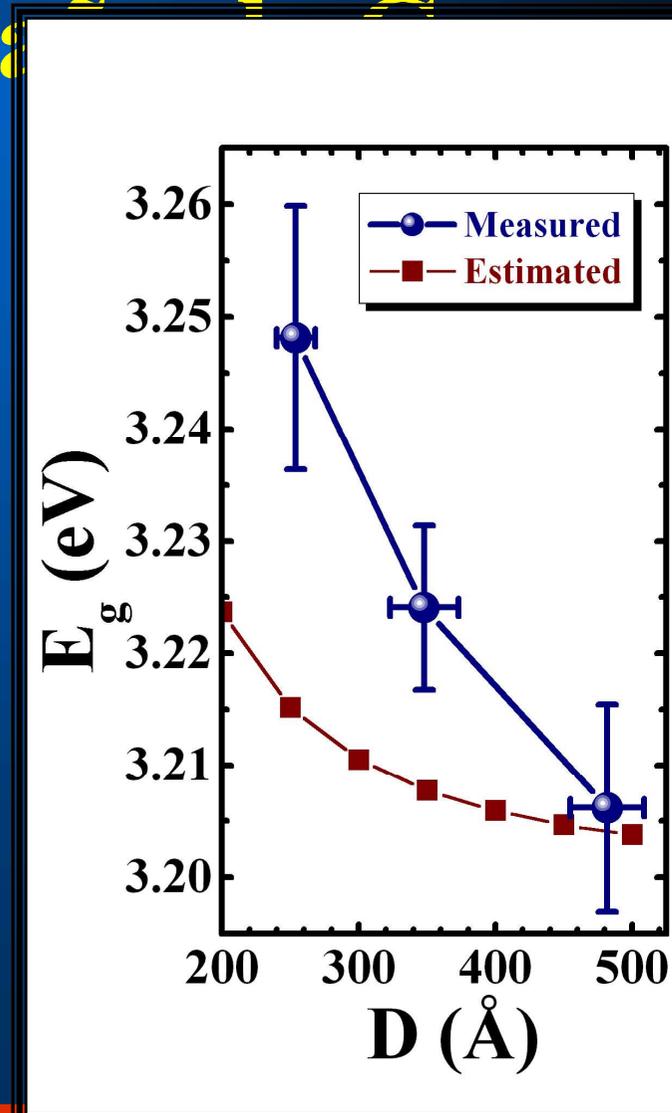
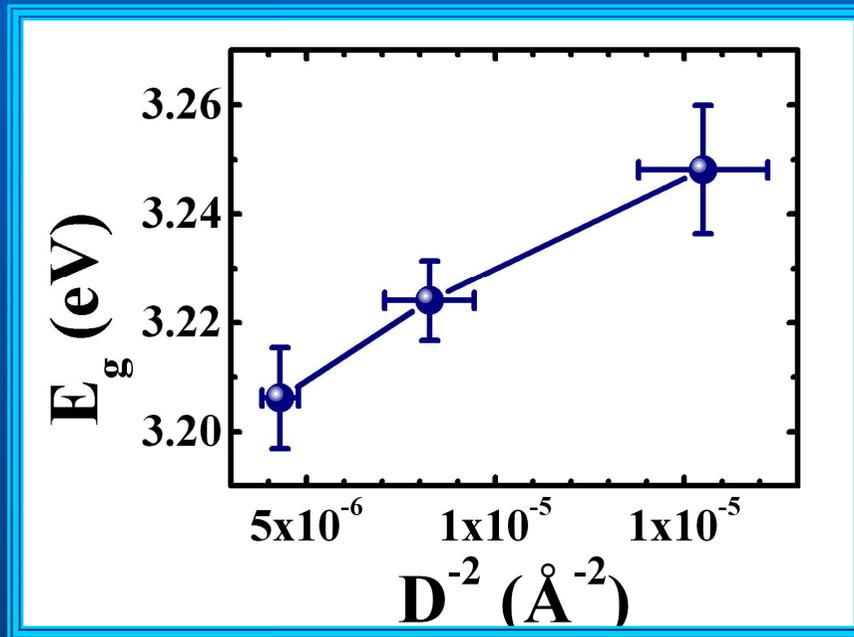
# ZnO: Reflectancia vs Temperatura de Deposición



$$E_g \propto \frac{1}{D^2} \Rightarrow QC$$

???

# ZnO: Borde de Absorción contra Tamaño



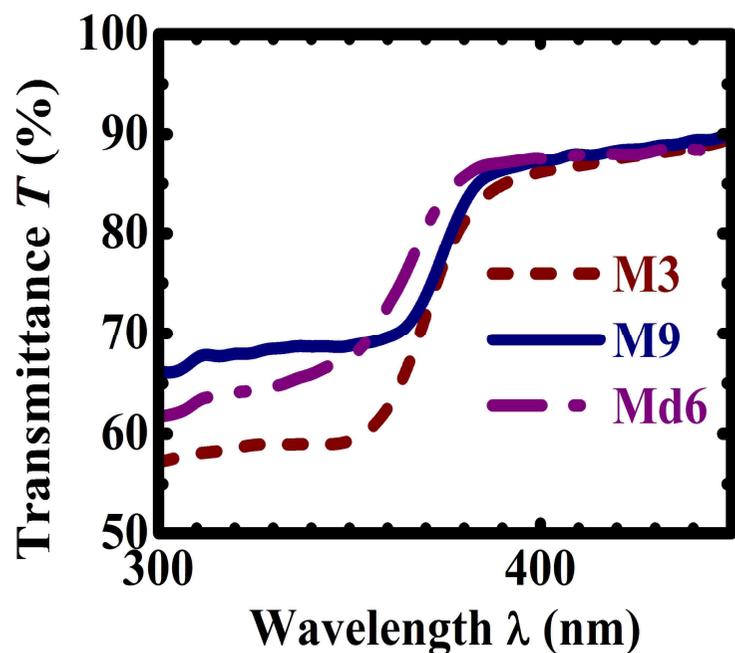
$$\Delta E_g \propto \frac{1}{D^2} \Rightarrow QC$$

# Al doped ZnO Sol-Gel Dip

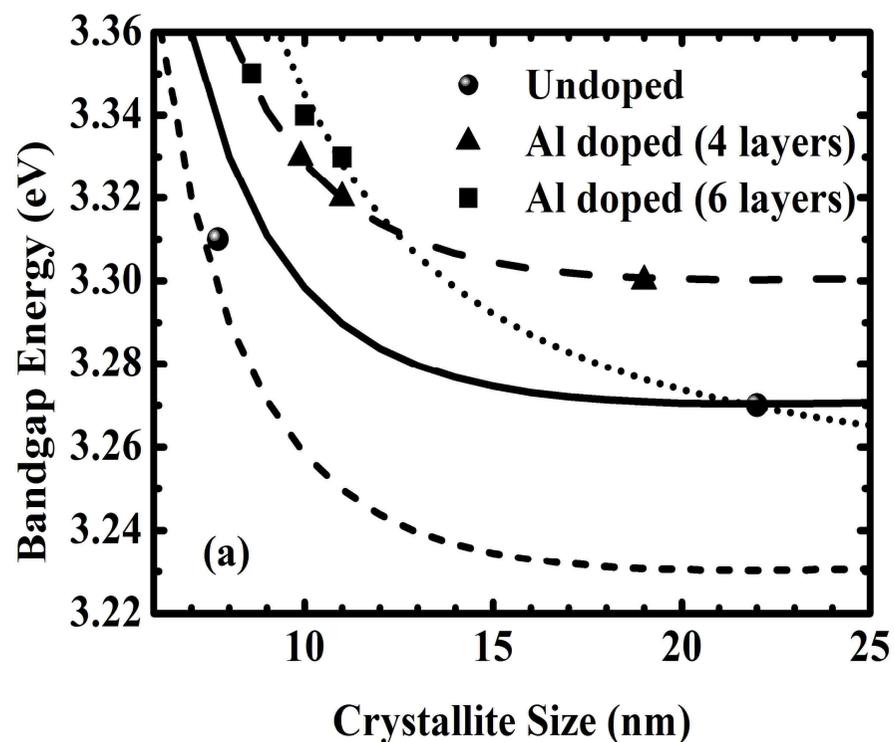
ating

M3, M9: undoped.

Md6: Al doped.

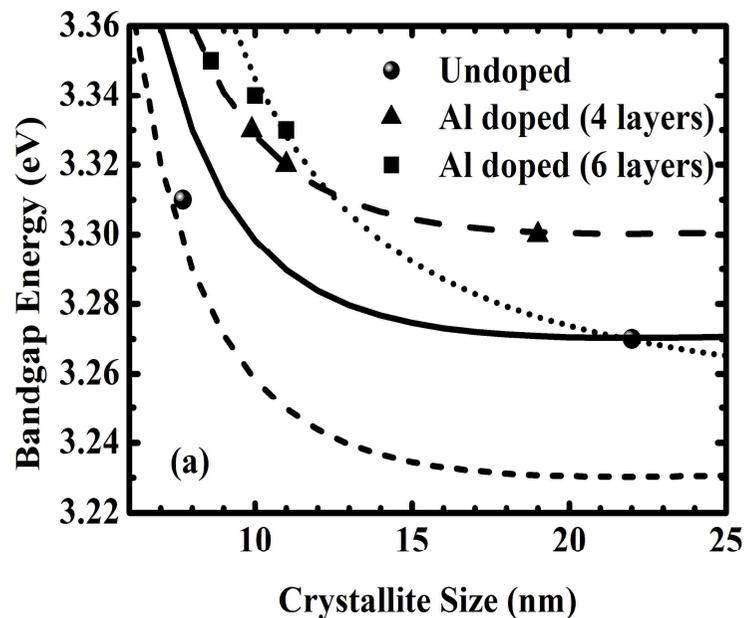


Al doped ZnO blue shifted more than undoped.



# Parámetros Confinamiento Cuántico

$$\Delta E = E(R) - E_g = E_b \left( \frac{\pi a_B}{R} \right)^2 - 3.6 E_b \left( \frac{a_B}{R} \right)$$



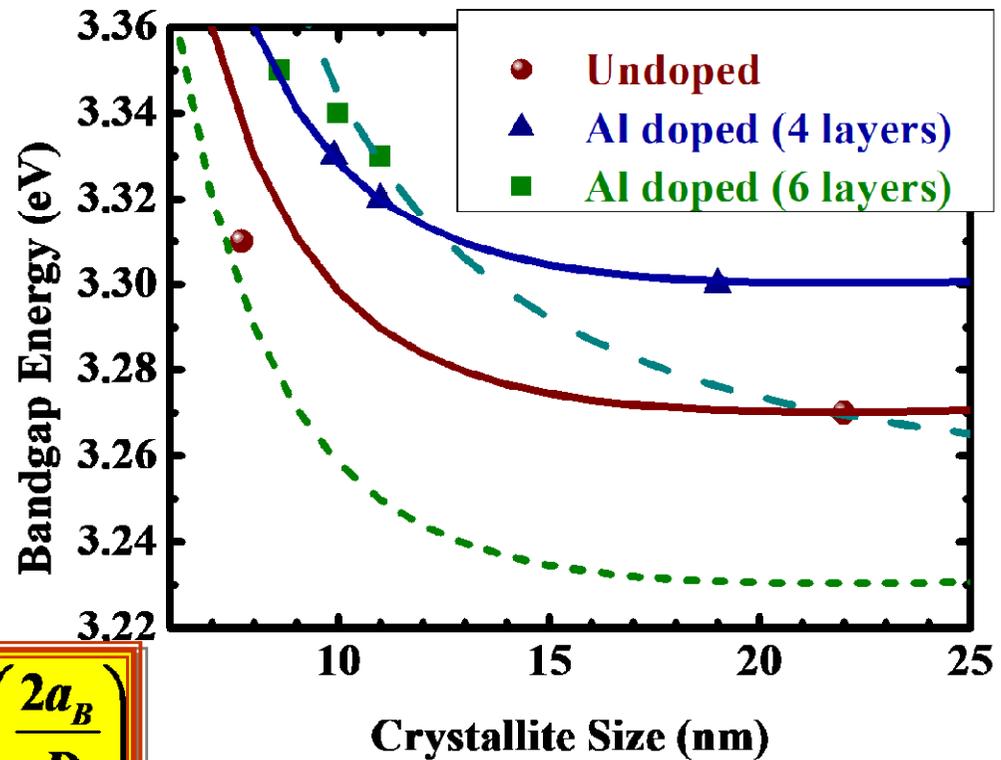
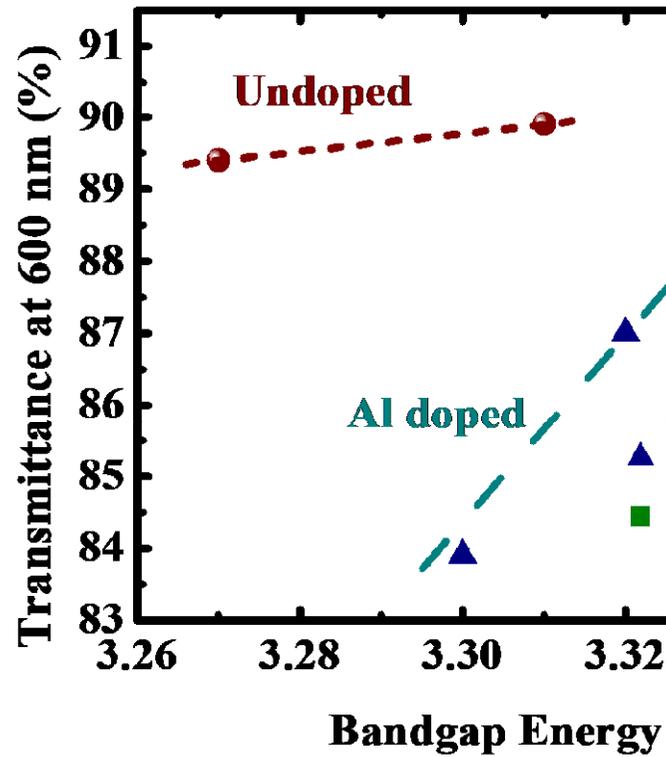
Binding Energy”

hr Radius”

ón de “Brus” (interacción e-h).

e Estados.

# Sumario de Resultados para sol-gel ZnO



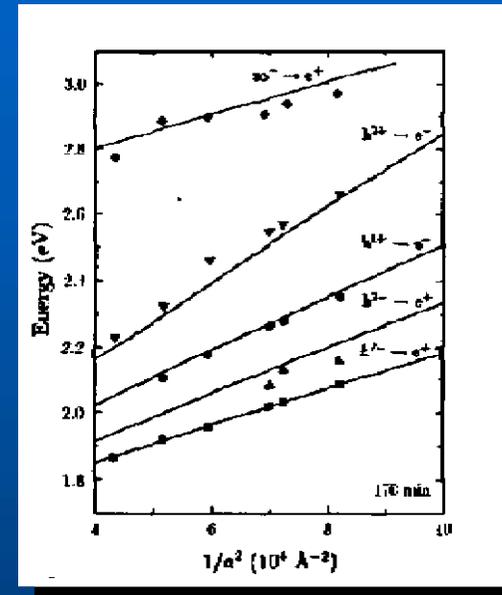
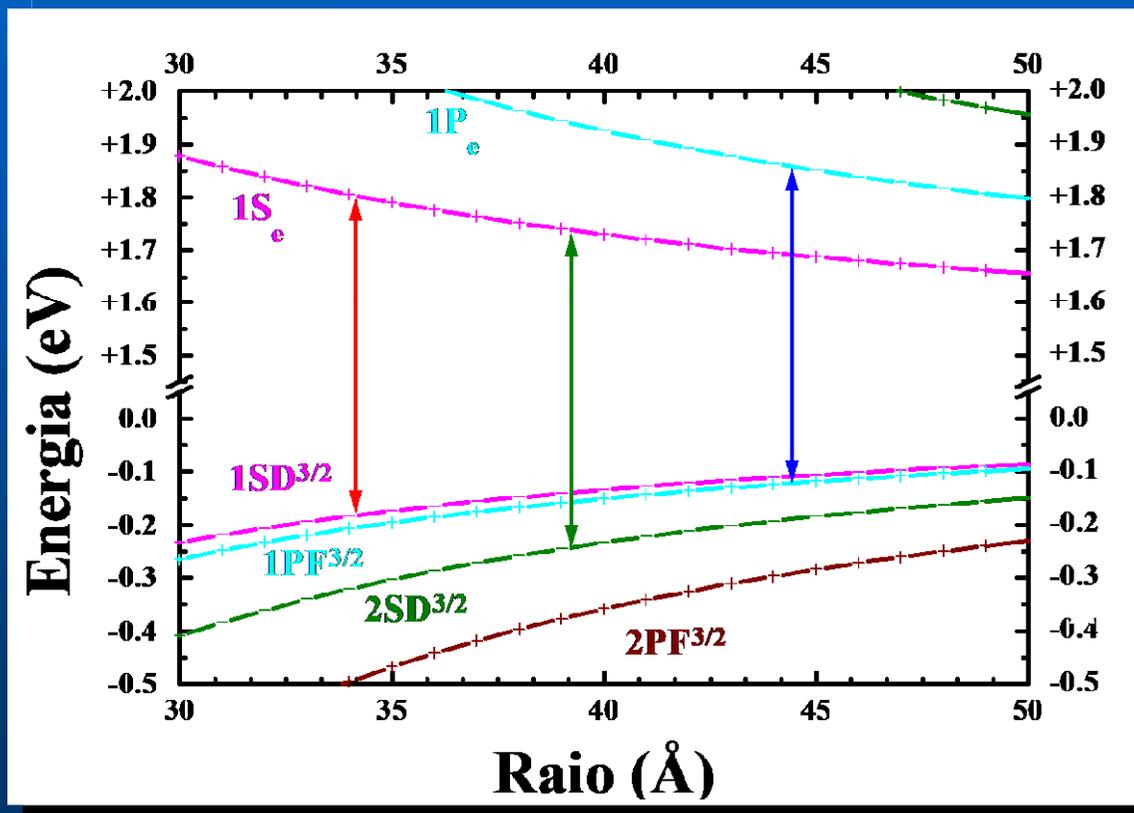
$$\Delta E_g \approx E_b \left( \frac{2\pi a_B}{D} \right)^2$$

$$-3.6 E_b \left( \frac{2a_B}{D} \right)$$

QC

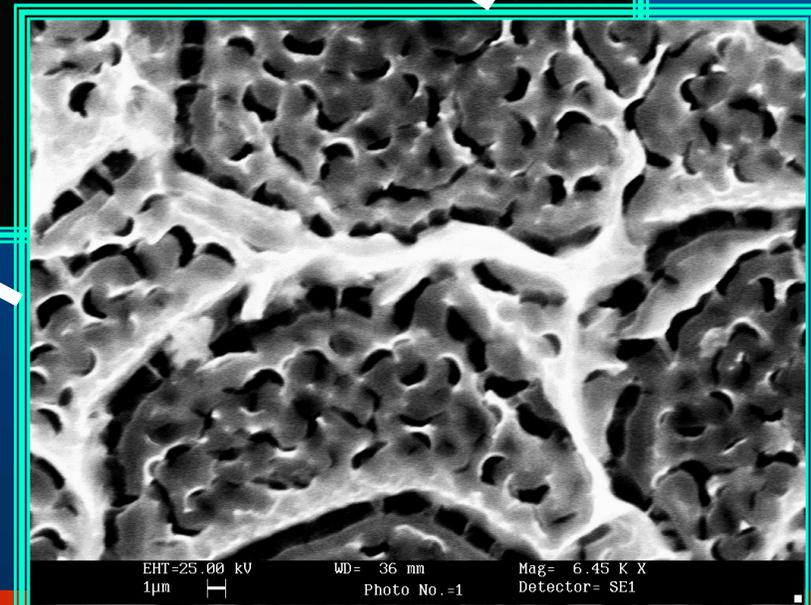
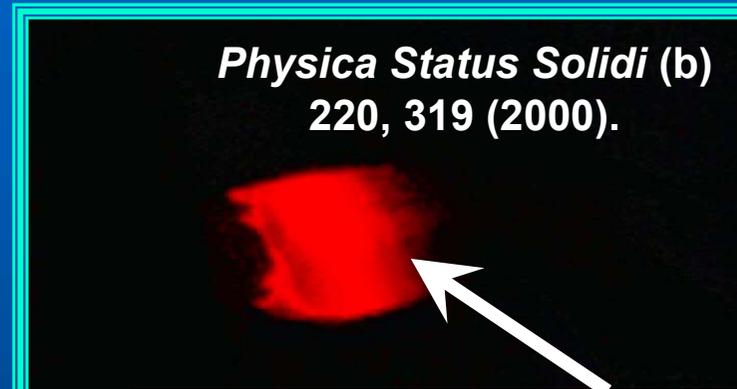
1<sup>st</sup> order e-h

# Estrutura Eletrônica.



*Phys. Lett.* 66 (1995) 439.

# Silicio Poroso ( $\pi$ -Si): Material Poroso Nanoestructurado



- 95 % electrónica basada en Silicio.
- Silicio: semiconductor indirecto
  - ▷ Mal emisor de luz
- Silicio Poroso emite luz roja.

# Si Poroso:

## Definición de $E_{\text{eff}}$

