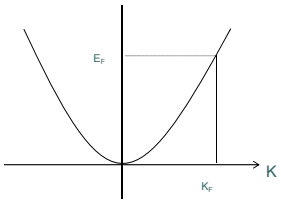
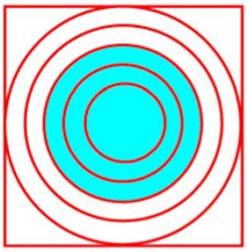
Fermi Surface

For free electrons, the constant energy surfaces are circular.

$$E(k) = \frac{\hbar^2 k_x^2}{2m}$$

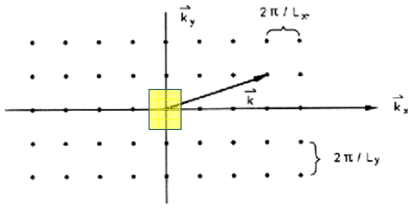


For a monovalent element, the volume of the Fermi surface is half that of the Brillouin zone:



$$\frac{a^2}{2} = \pi r^2$$

$$r = 0.4a$$



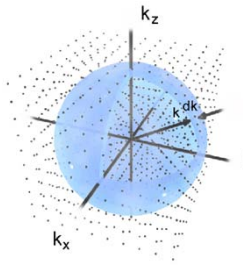
With periodic boundary conditions:

$$e^{ik_x L_x} = e^{ik_y L_y} = e^{ik_z L_z} = 1$$

$$k_x = \frac{2\pi n_x}{L_x}$$

$$k_y = \frac{2\pi n_y}{L_y}$$

$$k_z = \frac{2\pi n_z}{L_z}$$



2D k space:
Area per k point:

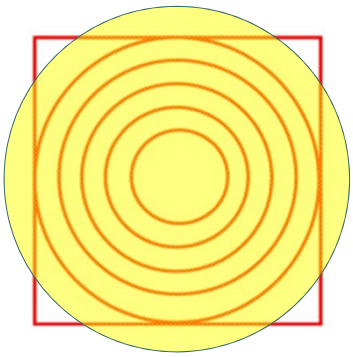
$$\frac{2\pi}{L_x}\frac{2\pi}{L_y}$$

3D k space:
Area per k point:

$$\frac{2\pi}{L_x}\frac{2\pi}{L_y}\frac{2\pi}{L_z} = \frac{8\pi^3}{V}$$

A region of k space of volume Ω will contain: $\frac{\Omega}{(\frac{8\pi^3}{V})} = \frac{\Omega V}{8\pi^3}$ allowed k values.

For divalent elements: free –electron model

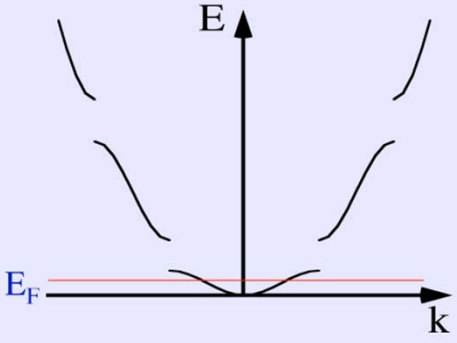


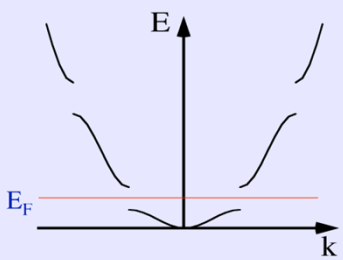
$$a^2 = \pi r^2$$

$$r = 0.56a$$

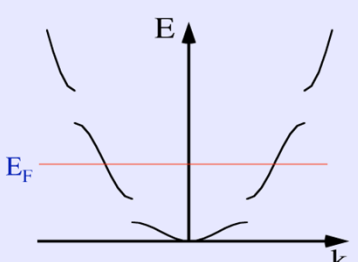
- as we increase the number of electrons per atom E_F moves up the dispersion relation:

1 electron per atom:





2 electrons per atom:

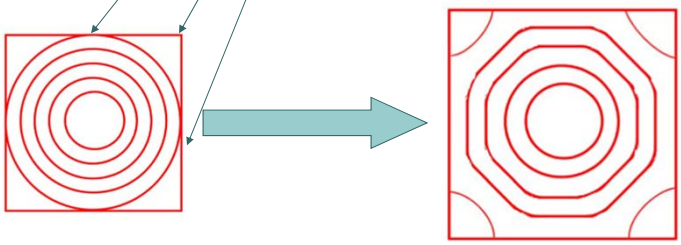


3 electrons per atom:

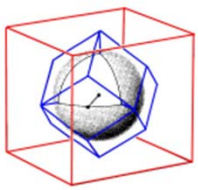
For nearly free electron:

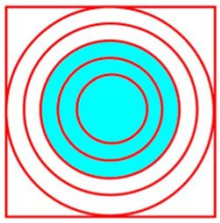
1. **Interaction of electron with periodic potential opens gap at zone boundary**
2. **Almost always Fermi surface will intersect zone Boundaries perpendicularly.**
3. **The total volume enclosed by the Fermi surface depends only on total electron concentration, not on interaction**

With the crystal potential, the energy inside the first Brillouin zone is *lower* close to the zone boundary. So the Fermi surface is extended *towards* the zone boundary as it gets close.



Alkali Metal Na, Cs: spherical Fermi surface

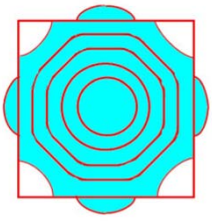




$$\frac{a^2}{2} = \pi r^2$$

$$r = 0.4a$$

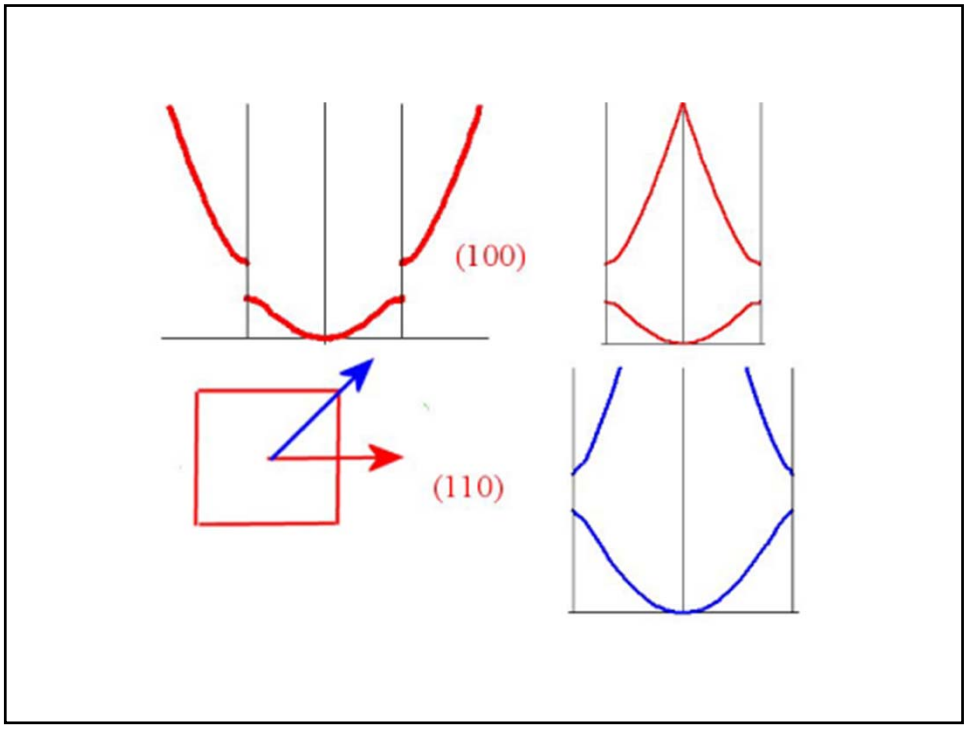
Alk. Earth metal: Be, Mg:: nearly spherical Fermi surface

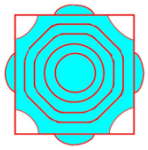


$$a^2 = \pi r^2$$

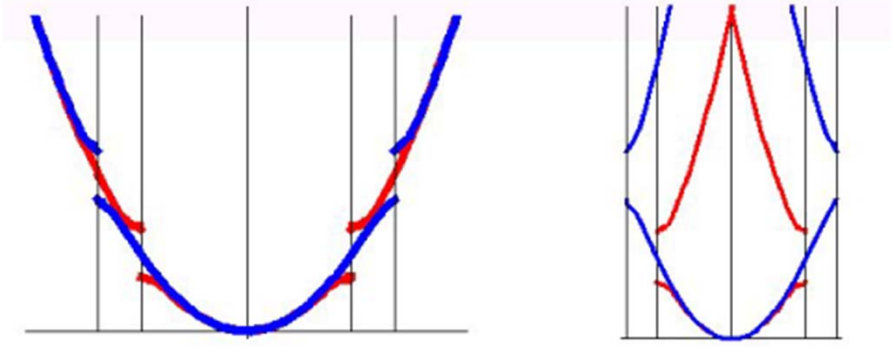
$$r = 0.56a$$

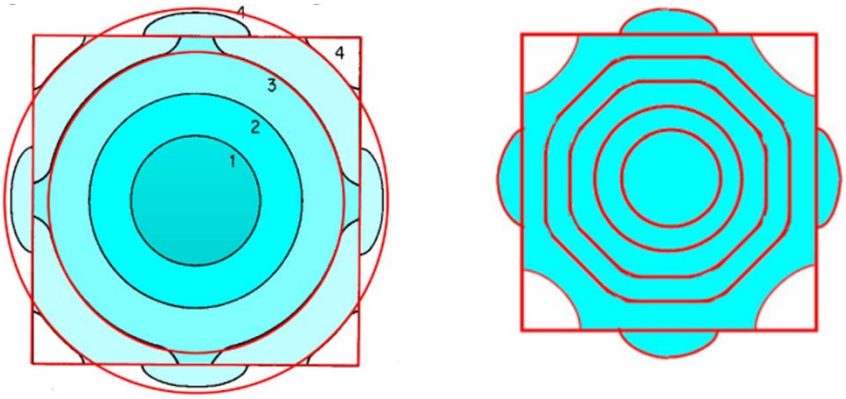
2D case



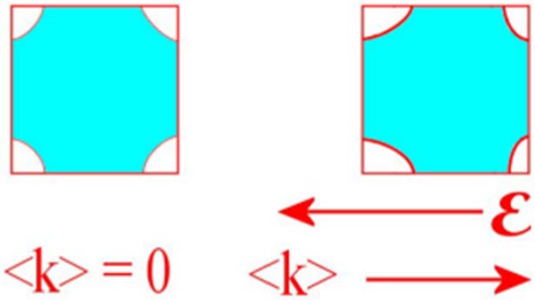


Consider a divalent metal in two dimensions. The area of k-space needed to accommodate all the electrons is equal to the area of the first Brillouin zone. We can see that the red states in the second band will start to be filled.

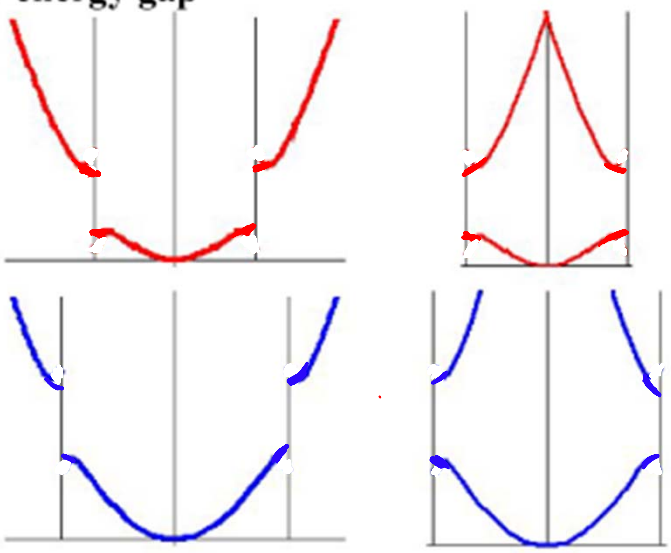




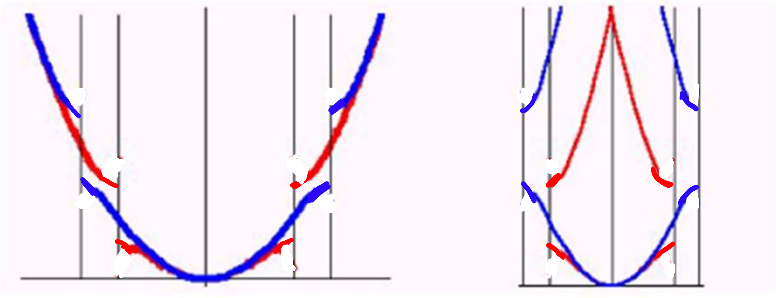
***Electric field*: a simple picture will show how the Fermi surface in a partly-filled zone will be shifted:**



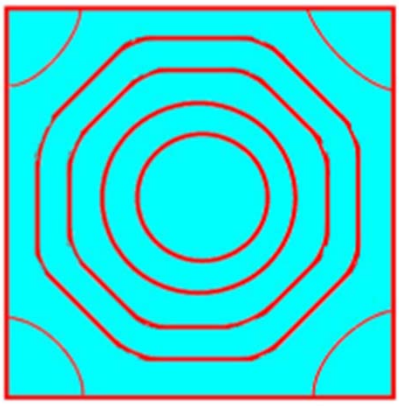
Take a larger energy gap



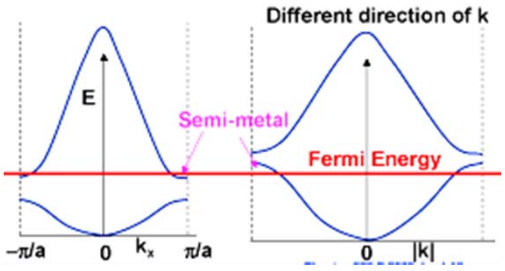
Superpose the curves

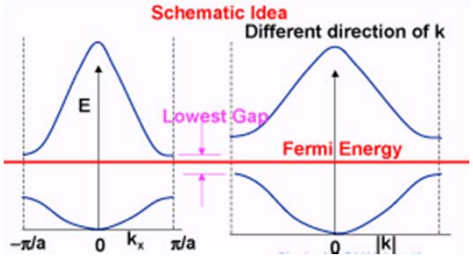


For a large gap, the whole of the first zone will be filled. This gives an insulator because if we apply a field to increase an electron's k vector, electrons at the zone boundary will be Bragg reflected back to the other side of the zone – there will be no net drift velocity. We only get current if we can excite some electrons into a higher energy band.

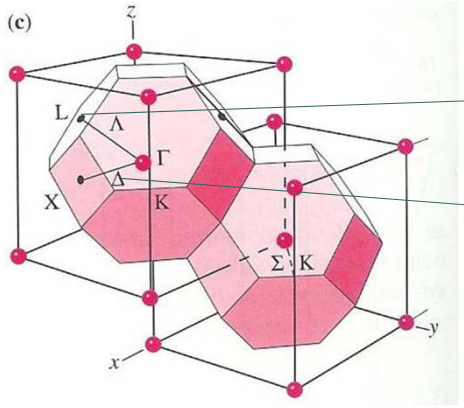


An insulator.



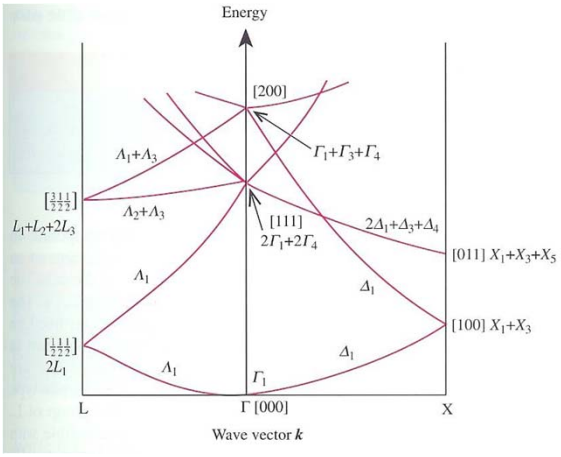


Brillouin Zone of Diamond and Zincblende Structure (FCC Lattice)

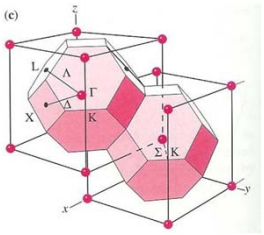


- Sign Convention
  - Zone Edge or surface : Latin alphabets
  - Interior of Zone: Greek alphabets
  - Center of Zone or origin: Γ

Band Structure of 3D Free Electron in FCC in reduced zone scheme



$E(k)=(\hbar^2/2m)\,(k_x^2+k_y^2+k_z^2)$



Notation:

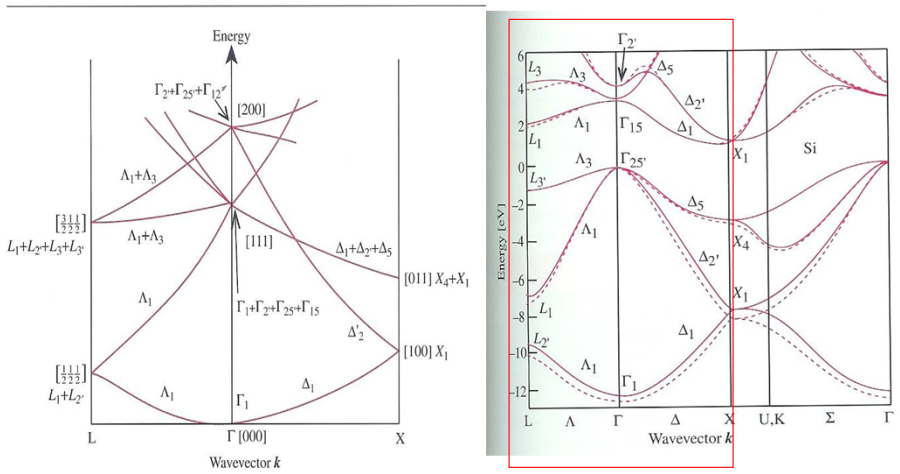
Δ<=>[100] direction

X<=>BZ edge along [100] direction

Λ<=>[111] direction

L<=>BZ edge along [111] direction

Comparison between Free Electron and Real Electron Band Structure of Si

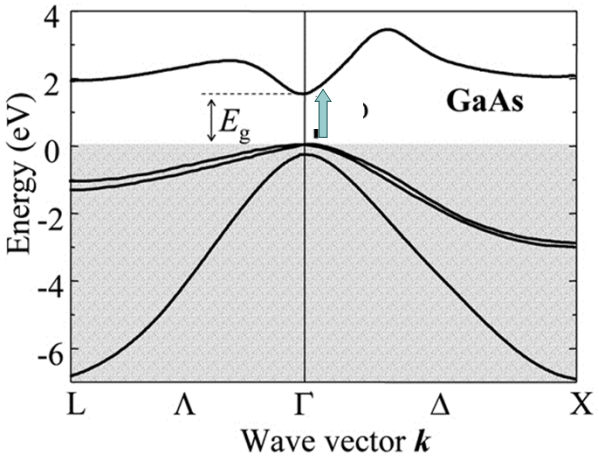


Properties of Semiconductors

Compound	Structure	Bandgap (eV)	e⁻ mobility (cm²/V-s)	h⁺ mobility (cm²/V-s)
Si	Diamond	1.11 (I)	1,350	480
Ge	Diamond	0.67 (I)	3,900	1,900
AlP	Sphalerite	2.43 (I)	80	---
GaAs		(D)	8,500	400
InSb		(D)	100,000	1,700
AlAs	Sphalerite	2.16 (I)	1,000	180
GaN	Wurtzite	3.4 (D)	300	---

$$\mu = \frac{v_d}{E} = \frac{e\tau}{m^*}$$

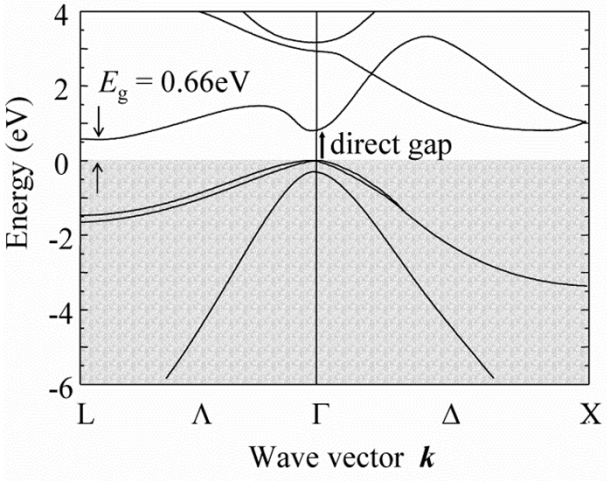
GaAs band structure



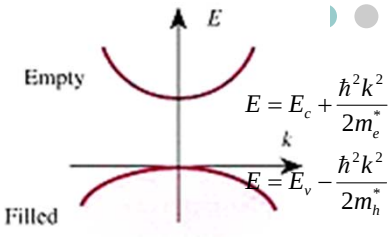
- Direct gap at 1.5 eV
- Very important optoelectronic material
- Strong absorption for $h\nu > E_g$

Chem 253, UC, Berkeley

Germanium band structure

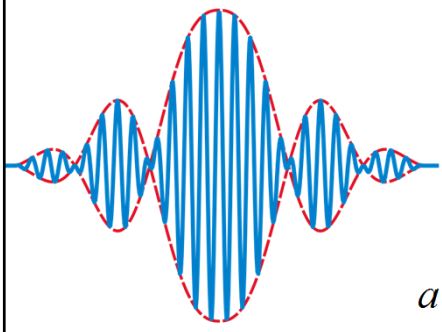


- Indirect gap at 0.66 eV
- Direct gap at 0.80 eV



Parabolic

Wave packet made of wavefunctions near a particular wavevector k



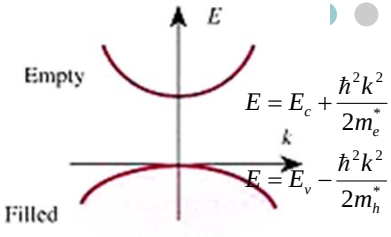
Motion of carrier in field:

Group velocity: transmission velocity of a wave packet

$$v_g = \frac{d\omega}{dk} = \frac{1}{\hbar}\frac{dE}{dk}$$

Acceleration:

$$a = \frac{dv_g}{dt} = \frac{1}{\hbar}\frac{d^2E}{dkdt} = \frac{1}{\hbar}\frac{d^2E}{dk^2}\frac{dk}{dt}$$



Parabolic

Wave packet made of wavefunctions near a particular wavevector k

Motion of carrier in field:

Group velocity: transmission velocity of a wave packet

$$v_g = \frac{d\omega}{dk} = \frac{1}{\hbar}\frac{dE}{dk}$$

Acceleration:

$$a = \frac{dv_g}{dt} = \frac{1}{\hbar}\frac{d^2E}{dkdt} = \frac{1}{\hbar}\frac{d^2E}{dk^2}\frac{dk}{dt}$$

Effective mass

$$p = m^* v = \hbar k$$

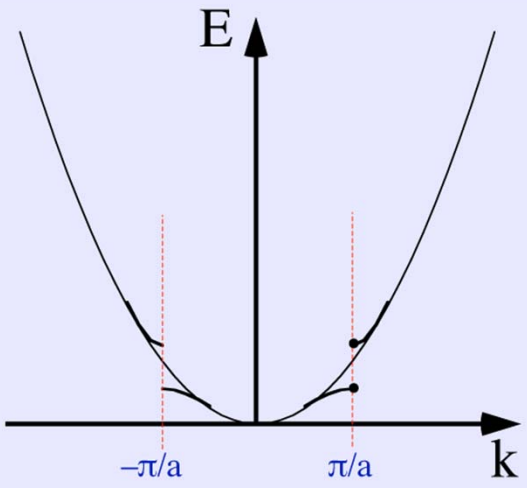
$$\frac{dv}{dt} = \frac{\hbar}{m^*}\frac{dk}{dt}$$

$$\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{d^2E}{dk^2}$$

Two possible energies at the BZ edge:

Standing waves:
zero group velocity

$$\rightarrow \frac{dE}{dk} = 0$$



$$\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{d^2E}{dk^2}$$

Positive m*: the band has upward curvature $\frac{d^2E}{dk^2} > 0$

If the energy in a band depend only weakly on k, then m* very large

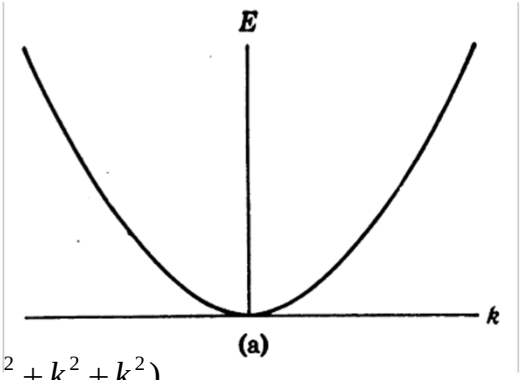
$m^*/m >> 1$ When $\frac{d^2E}{dk^2}$ very small.

Heavy carrier

Free-electrons

$m^* = m_e$

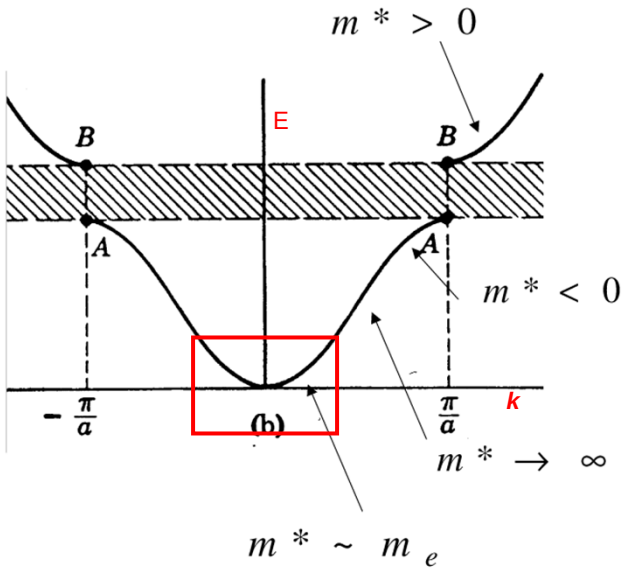
$$\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{d^2E}{dk^2}$$



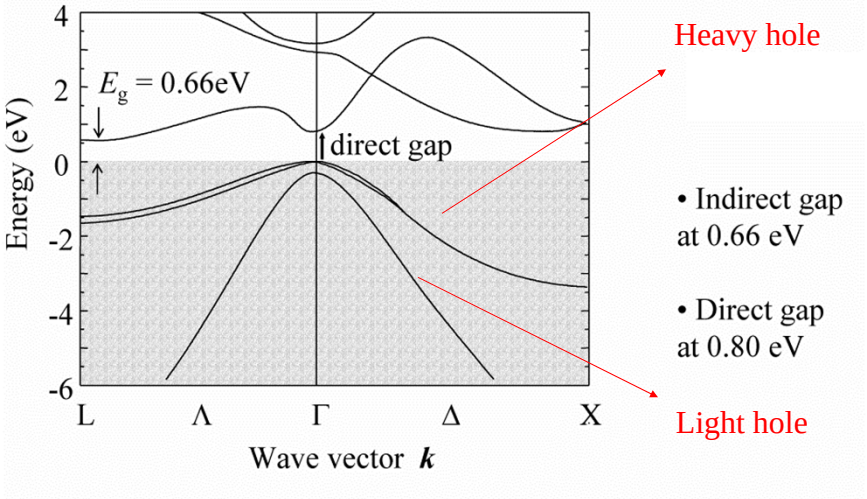
$$E(k) = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2)$$

• Periodic Potential

$$\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{d^2E}{dk^2}$$



Germanium band structure

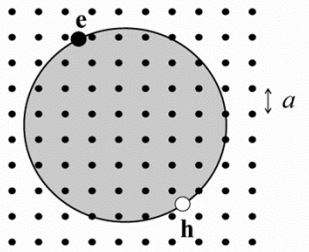


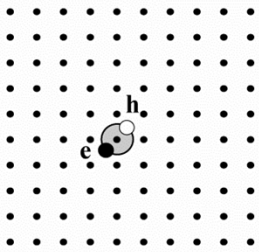
Group	Material	Electron m_e	Hole m_h
IV	Si (300K)	1.08	0.56
	Ge	0.55	0.37
III-V	GaAs	0.067	0.45
	InSb	0.013	0.6
II-VI	ZnO	0.29	1.21
	ZnSe	0.17	1.44

Excitons

- The annihilation of a photon in exciting an electron from the valence band to the conduction band in a semiconductor can be written as an equation: $\hbar\omega \rightarrow e+h$.
- Since there is a *Coulomb attraction* between the electron and hole, the photon energy required is lowered than the band gap by this attraction
- To correctly calculate the absorption coefficient we have to introduce a two-particle state consisting of an electron attracted to a hole known as an exciton

Excitons

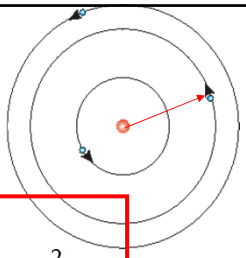




Free (Wannier)
radius >> *a*
small binding energy
moves freely through crystal

Tightly-bound (Frenkel)
radius ~ *a*
large binding energy
localized on one lattice site

- Excitons represent *the elementary excitation* of a semiconductor. In the ground state the semiconductor has only filled or empty bands. The simplest excitation is to excite one electron from a filled band to an empty band and so creating an electron and a hole
- Exciton is *neutral* over all but carries an *electric dipole moment* and therefore can be excited by *either a photon or an electron*



$$\frac{m_e v^2}{r} = \frac{e^2}{r^2}$$

$$v = \frac{nh}{2\pi m_e r}$$

$$r_n = \frac{n^2 h^2}{4\pi^2 m_e e^2} = n^2 a_0$$

r_1=Bohr radius =a_0=0.529 Å

$$E = \frac{1}{2} m_e v^2 + (-\frac{e^2}{r})$$
$$= \frac{1}{2}(\frac{e^2}{r}) - \frac{e^2}{r}$$
$$= -\frac{e^2}{2r}$$

$$E_n = -\frac{e^2}{2r_n} = -\frac{2\pi^2 m_e e^4}{n^2 h^2} = -\frac{k}{n^2}$$

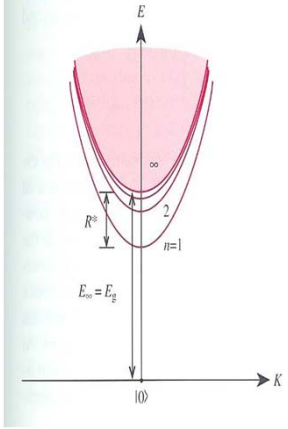
k= 13.606 eV

H $r_n = \frac{n^2 h^2}{4\pi^2 m_e e^2} = n^2 a_0$

$E_n = -\frac{e^2}{2r_n} = -\frac{2\pi^2 m_e e^4}{n^2 h^2}$

Excitons

$$E(k) = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2)$$



$$U(r) = -\frac{e^2}{\varepsilon r}$$

$$E_n = E - \frac{\mu e^4}{2\hbar^2 \varepsilon^2 n^2}$$

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

Reduced mass

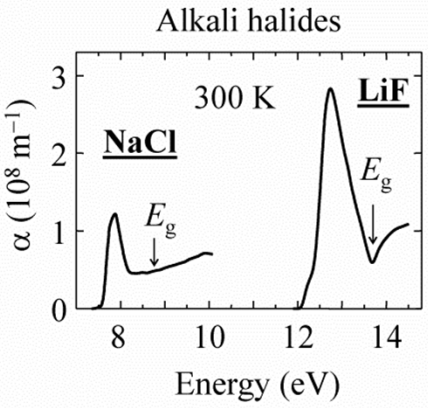
Binding energy:

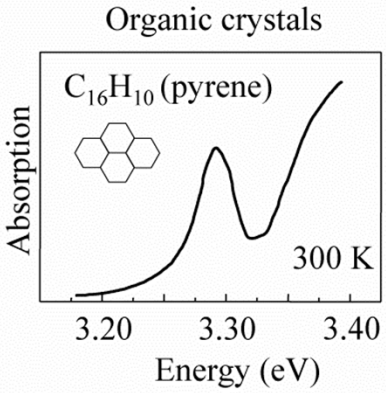
$$E_n = E - \frac{\mu e^4}{2\hbar^2 \varepsilon^2 n^2} = 13.6ev \times \frac{\mu}{\varepsilon^2 m_e}$$

Exciton Bohr Radius:

$$r_{ex} = \frac{\varepsilon h^2}{4\pi^2 e^2}(\frac{1}{m_e^*} + \frac{1}{m_h^*}) = 0.529\frac{\varepsilon m_e}{\mu}$$

Frenkel excitons





	E_g(eV)	R_X (eV)
NaCl	8.8	0.9
LiF	13.7	1.9

$$R_x = E_n = 13.6ev \times \frac{\mu}{\varepsilon^2 m}$$

$$r = 0.529 \frac{\varepsilon m}{\mu}$$

Also: Rare gas crystals (solid Ne, Ar, Kr, Xe)

Semiconductor	Energy gap (eV) at 273 K	Effective mass m*/m		Dielectric constant
		Electrons	Holes	
Ge	0.67	0.2	0.3	16
Si	1.14	0.33	0.5	12
InSb	0.16	0.013	0.6	18
InAs	0.33	0.02	0.4	14.5
InP	1.29	0.07	0.4	14
GaSb	0.67	0.047	0.5	15
GaAs	1.39	0.072	0.5	13

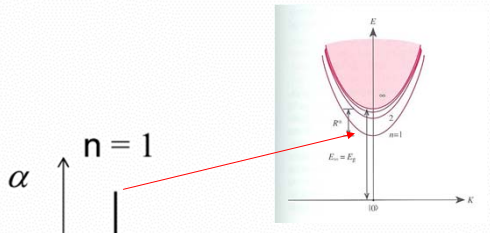
Exciton

$$E_n = 13.6ev \times \frac{\mu}{\varepsilon^2 m}$$

$$r = 0.529 \frac{\varepsilon m}{\mu}$$

Semiconductor	E_g	$\ldots\ldots\mu / m$ $(m_e^* / m_e ; m_h^* / m_h)$	R_x or E_{ex} meV	r_{ex} nm
Si	1.11	0.33; 0.50	14.7	4.9
Ge	0.67	0.2; 0.3	4.15	17.7
GaAs	1.42	0.0616 (0.066, 0.5)	4.2	11.3
CdSe	1.74	(0.13, 0.45)	15	5.2
Bi	0	0.001	small	>50
ZnO	3.4	(0.27, ?)	59	3
GaN	3.4	(0.19, 0.60)	25	11

Free exciton absorption

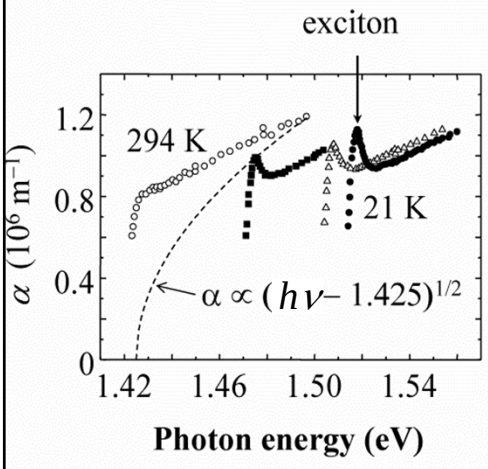


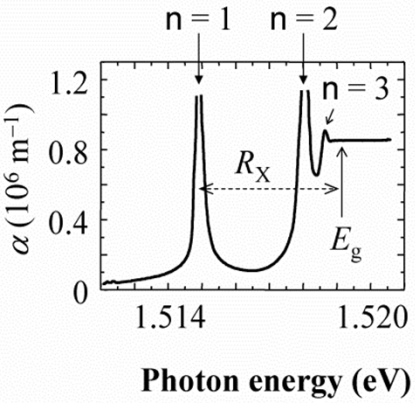
Exciton binding energy

- Hydrogenic series of lines satisfying : $h\nu = E_g - R_X / n^2$
- enhanced absorption for $h\nu > E_g$
- only observed when $T \leq (R_X / k_B)$ otherwise dissociates

Related to DOS

Excitons in bulk GaAs





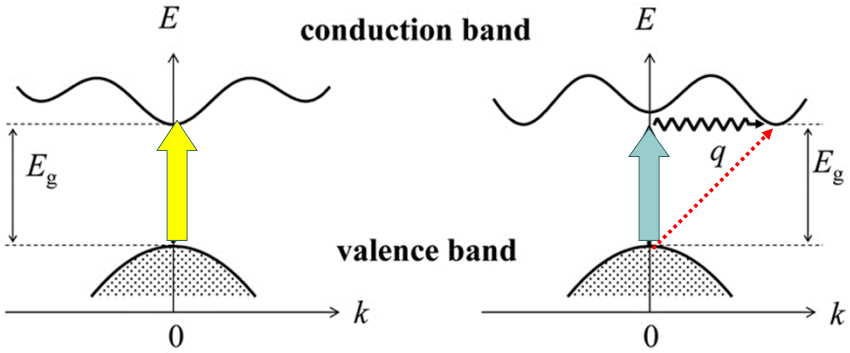
- standard purity sample
- T = 21 K – 294 K

- ultra pure sample
- T = 1.2 K
- R_X = 4.2 meV

Direct and Indirect absorption

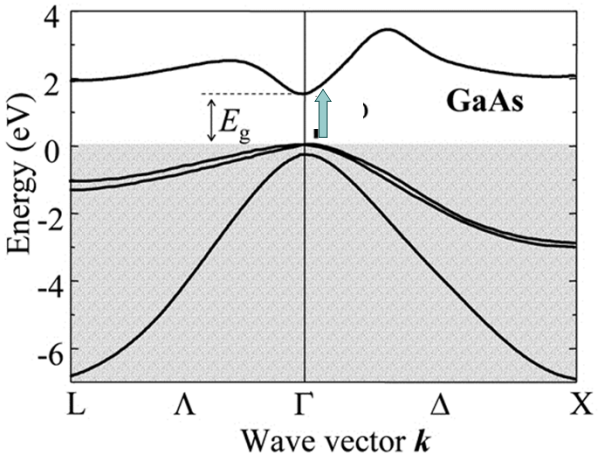
(a) Direct band gap:
C.B. minimum at $k = 0$

(b) Indirect band gap
C.B. minimum at $k \neq 0$



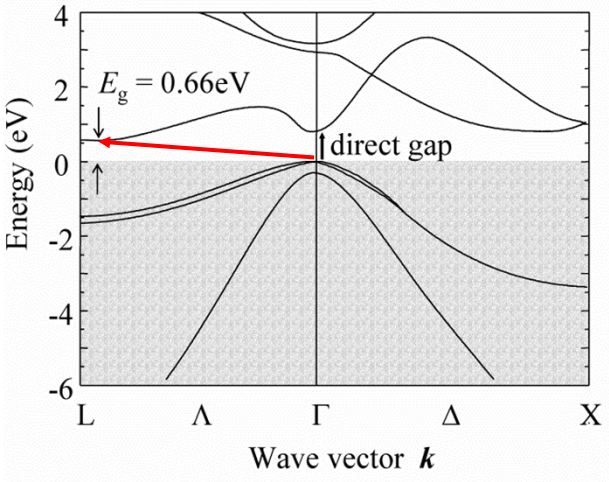
- $k_{photon} = 2\pi/\lambda \sim 10^7$ m^{-1} negligible compared to B.Z. size $\pi/a \sim 10^{11}$ m^{-1}
- Transitions appear as vertical lines on $E - k$ diagrams
- Phonon needed to conserve momentum for indirect gap materials
- Indirect absorption 2nd order process, therefore low probability

GaAs band structure

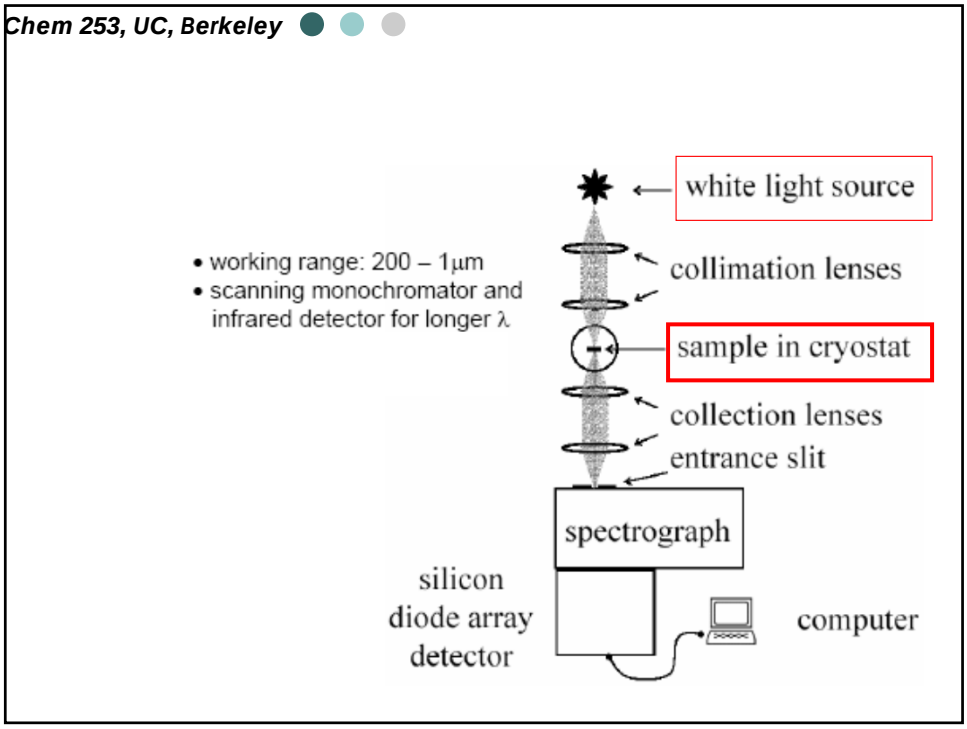


- Direct gap at 1.5 eV
- Very important optoelectronic material
- Strong absorption for $h\nu > E_g$

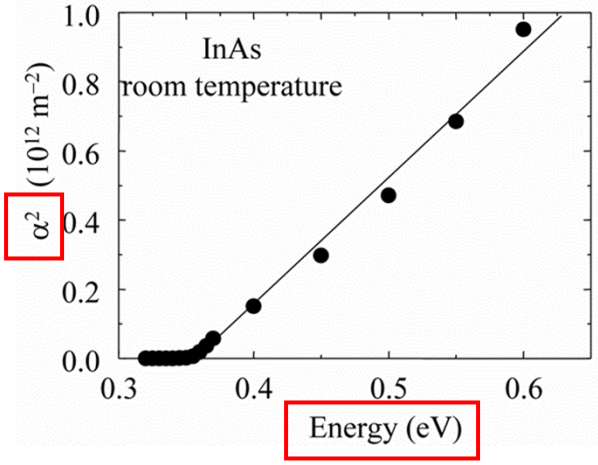
Germanium band structure



- Indirect gap at 0.66 eV
- Direct gap at 0.80 eV



InAs band edge absorption

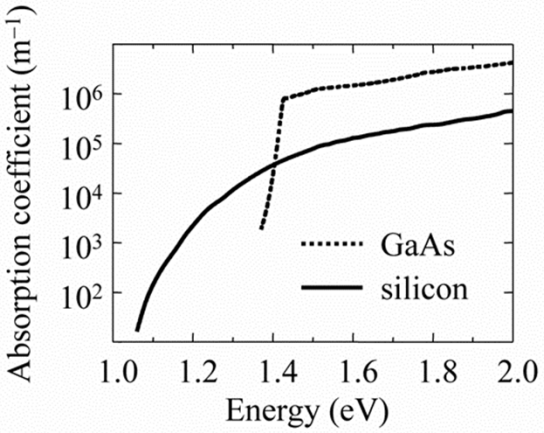


InAs is a direct gap III–V semiconductor with $E_g = 0.35$ eV

$h\nu < E_g$: $\alpha = 0$

$h\nu > E_g$:
$\alpha \propto (h\nu - E_g)^{1/2}$

Direct versus indirect absorption

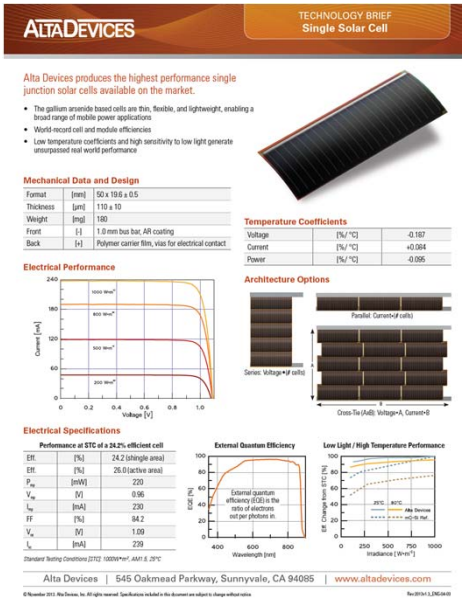


- Direct absorption is much stronger than indirect absorption
- Silicon has **indirect** gap at 1.1 eV
- GaAs has **direct** gap at 1.4 eV

Implication in solar cell

Chem 253, UC, Berkeley

Thin film PV


ALTADEVICES

TECHNOLOGY BRIEF
Single Solar Cell

Alta Devices produces the highest performance single junction solar cells available on the market.

- The gallium arsenide based cells are thin, flexible, and lightweight, enabling a broad range of mobile power applications
- World-record cell and module efficiencies
- Low temperature coefficients and high sensitivity to low light generate unsurpassed real world performance

Mechanical Data and Design

Format	[mm]	50 x 19.6 ± 0.5
Thickness	[µm]	110 ± 10
Weight	[mg]	160
Front	[-]	1.0 mm bus bar, AR coating
Back	[+]	Polymer carrier film, vias for electrical contact

Temperature Coefficients

Voltage	[%/ °C]	-0.187
Current	[%/ °C]	+0.084
Power	[%/ °C]	-0.095

Electrical Performance

Architecture Options

Parallel: Current=∑(# cells)

Series: Voltage=∑(# cells)

Cross-Tie (Adj): Voltage=A, Current=B

Electrical Specifications

Performance at STC of a 24.2% efficient cell

Eff.	[%]	24.2 (shingle area)
Eff.	[%]	26.0 (active area)
P_{mp}	[mW]	220
V_{mp}	[V]	0.96
I_{sc}	[mA]	230
FF	[%]	84.2
V_{oc}	[V]	1.09
I_{sc}	[mA]	239

Standard Testing Conditions [STC]: 1000W/m², AM1.5, 25°C

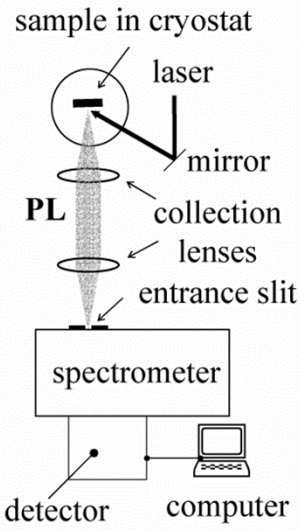
External Quantum Efficiency

Low Light / High Temperature Performance

Alta Devices | 545 Oakmead Parkway, Sunnyvale, CA 94085 | www.altadevices.com

Si PV

Photoluminescence spectroscopy

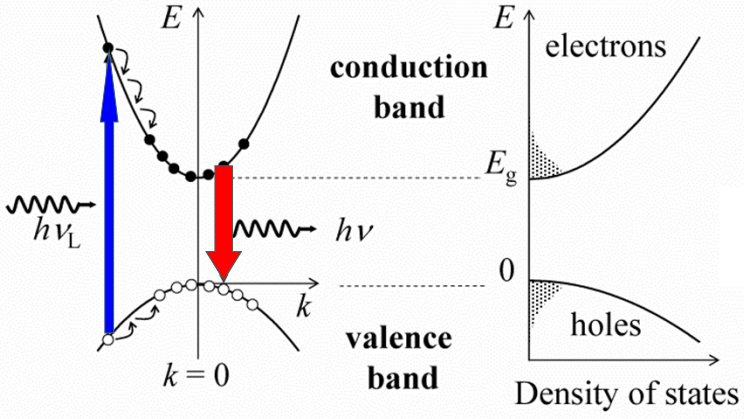


Photoluminescence (PL) spectroscopy
- fixed frequency laser, measure spectrum by scanning spectrometer

PL excitation spectroscopy (PLE)
- detect at peak emission, vary laser frequency
- effectively measures absorption

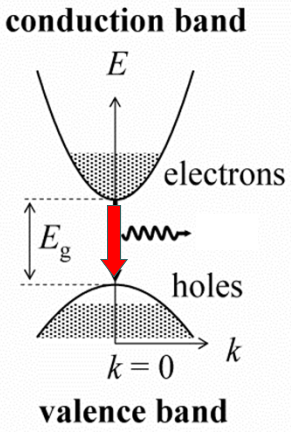
Time-resolved PL spectroscopy
- short pulse laser + fast detector
- measure lifetimes, relaxation processes

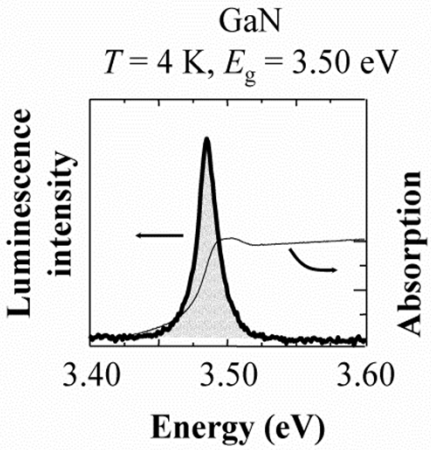
Photoluminescence



- Excite using laser with photon energy > E_g
- electrons and holes relax to the bottom of their bands
- thermal distributions formed according to **statistical mechanics**
- emission from E_g to top of carrier distributions

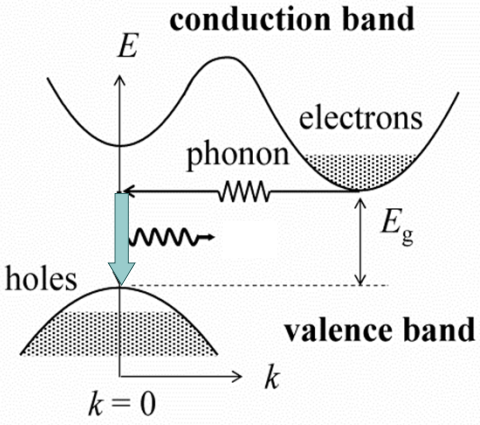
Direct gap materials





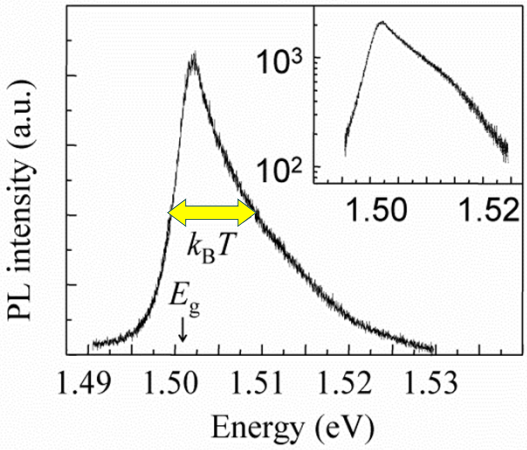
- Strong emission at the band gap
- most III-V and II-VI semiconductors
- linewidth ≥ k_BT

Indirect gap materials



- Low emission probability (2nd order process)
- Long radiative lifetime ⇒ low radiative quantum efficiency
- diamond, silicon, germanium, AlAs

Classical (Boltzmann)Statistics

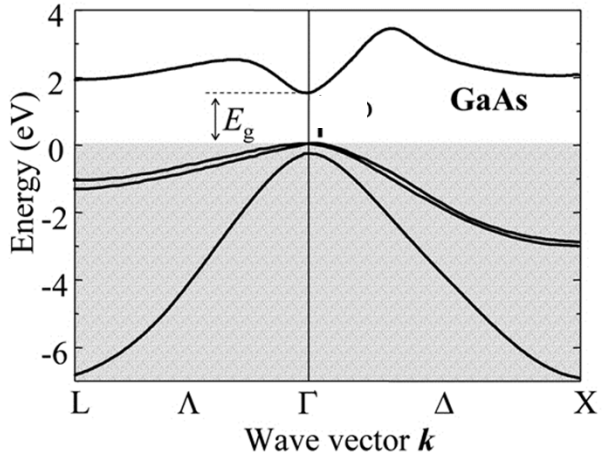


GaAs
$T = 100$ K
$k_BT = 8.6$ meV
$E_g = 1.501$ eV

Fermi's golden rule
$Rate \propto |M|^2 \rho(h\nu)$

- $I(E) \propto$ Density of states $\times f_e(E) f_h(E)$
- PL rises sharply at E_g, then decays exponentially. Linewidth ~ k_BT

GaAs band structure



- Direct gap at 1.5 eV
- Very important optoelectronic material
- Strong absorption for $h\nu > E_g$

Fermi's Golden Rule:

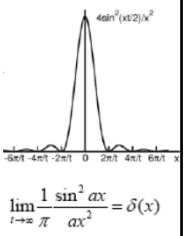
•Time-dependent perturbation theory: treat excitations which depend on time
•**Optical transition**: view the solid with unperturbed Hamiltonian H_0 as being perturbed by the time-dependent EM field H'(t) generated by the incident photon flux.

$$H = H_0 + H'(t)$$

Transition Rate

$$\Gamma_{ml} = \frac{2\pi}{\hbar}\left|\langle m|H'|l\rangle\right|^2 \delta(E_l - E_m - \hbar\omega)$$

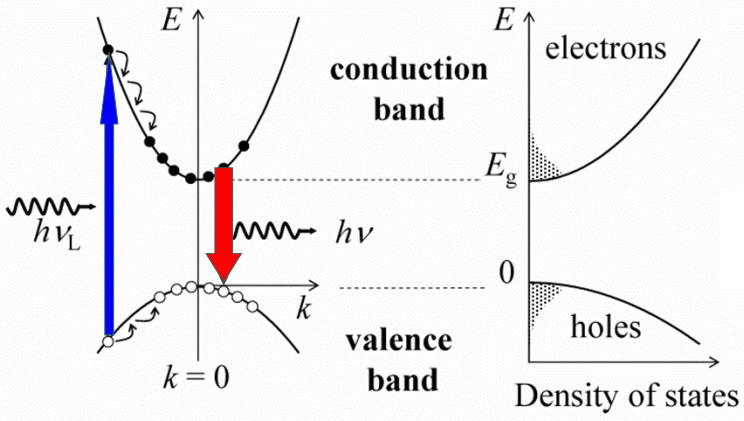
$\hbar\omega$ is the photon energy
+: emission
-: absorption



$$\lim_{t\to\infty}\frac{1}{\pi}\frac{\sin^2 ax}{ax^2} = \delta(x)$$

Atkins, Molecular Quantum Mechanics, Oxford

Photoluminescence



- Excite using laser with photon energy > E_g
- electrons and holes relax to the bottom of their bands
- thermal distributions formed according to **statistical mechanics**
- emission from E_g to top of carrier distributions

Fermi's Golden Rule:

$$\Gamma = \sum_{m,l} \Gamma_{ml} = \sum_{m,l} \frac{2\pi}{\hbar} |\langle m|\mathsf{H}'|l\rangle|^2 \delta(\mathsf{E}_l - \mathsf{E}_m - \hbar\omega)$$

$$\simeq \frac{2\pi}{\hbar} |\langle m|\mathsf{H}'|l\rangle|^2 \sum_{m,l} \delta(\mathsf{E}_l - \mathsf{E}_m - \hbar\omega)$$

Assume the state m and l are the valence and conduction band states, then $\langle m|H'|l\rangle = \langle v|H'|c\rangle = H'_{vc}$

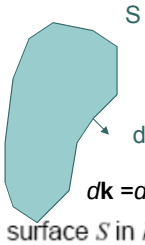
Define: Joint density of states

$$\rho_{vc}(\hbar\omega) = \frac{2}{8\pi^3} \int dk \delta(\mathsf{E}_c(k) - \mathsf{E}_v(k) - \hbar\omega)$$

$$\Gamma = \frac{2\pi}{\hbar} |\mathsf{H}'_{vc}|^2 \rho_{vc}(\mathsf{E}_c(k) - \mathsf{E}_v(k) - \hbar\omega)$$

Fermi's Golden Rule:

S is the surface of all possible direct optical transitions with hω = Ec - Ev



dk = *dSdk*n

energy surface *S* in *k*-space

Let's introduce an energy surface *S* in *k*-space such that $E_c - E_v = \hbar\omega$

$$d\mathsf{E} = |\nabla_k \mathsf{E}| dk_n$$

so

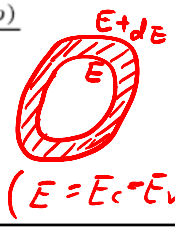
$$|\nabla_k(\mathsf{E}_c - \mathsf{E}_v)| dk_n = d(\mathsf{E}_c - \mathsf{E}_v)$$

and thus

$$d\mathbf{k} = dS\, dk_n = dS \left\{ \frac{d(\mathsf{E}_c - \mathsf{E}_v)}{|\nabla_k(\mathsf{E}_c - \mathsf{E}_v)|} \right\}$$

The joint density of states is then $\rho_{vc}(\hbar\omega) = \frac{2}{8\pi^3} \int dk \delta(E_c(k) - E_v(k) - \hbar\omega)$

$$\rho_{vc}(\hbar\omega) = \frac{2}{8\pi^3} \int_{k\text{-space}} \frac{dS\, d(\mathsf{E}_c - \mathsf{E}_v)\, \delta(\mathsf{E}_c - \mathsf{E}_v - \hbar\omega)}{|\nabla_k(\mathsf{E}_c - \mathsf{E}_v)|}$$



Integrating over $d(\mathsf{E}_c - \mathsf{E}_v)$ gives

$$\rho_{vc}(\hbar\omega) = \frac{2}{8\pi^3} \int_{k\text{-space}} \frac{dS}{|\nabla_k(\mathsf{E}_c - \mathsf{E}_v)|_{\mathsf{E}_c - \mathsf{E}_v = \hbar\omega}}$$

Fermi's Golden Rule:

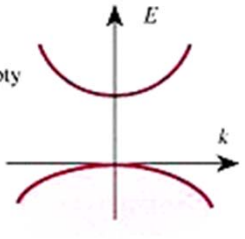
At critical point where

$\nabla_k(\mathsf{E}_c - \mathsf{E}_v) \rightarrow 0$

Large JDOS contribution.

$$E = E_c + \frac{\hbar^2 k^2}{2m_e^*}$$

$$E = E_v - \frac{\hbar^2 k^2}{2m_h^*}$$

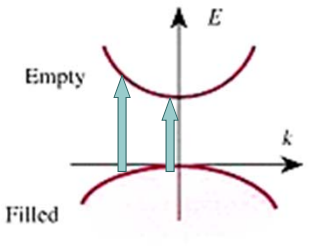


$$\mathsf{E}_c(k) - \mathsf{E}_v(k) = \mathsf{E}_g + \frac{\hbar^2 k^2}{2}\left(\frac{1}{m_c^*} + \frac{1}{m_v^*}\right) = \mathsf{E}_g + \frac{\hbar^2 k^2}{2m_r^*}$$

the gradient of $\mathsf{E}_c - \mathsf{E}_v$ is $\nabla_k(\mathsf{E}_c - \mathsf{E}_v) = \frac{\hbar^2 k}{m_r^*}$

$$\rho_{vc}(\hbar\omega) = \frac{2}{8\pi^3}\int \frac{dS}{|\nabla_k(\mathsf{E}_c - \mathsf{E}_v)|_{\mathsf{E}_c - \mathsf{E}_v = \hbar\omega}} = \frac{2}{8\pi^3}\left[\frac{4\pi k^2}{\frac{\hbar^2 k}{m_r^*}}\right]_{\mathsf{E}_c - \mathsf{E}_v = \hbar\omega} = \frac{m_r^*}{\pi^2\hbar^2}k$$

Fermi's Golden Rule:



To evaluate k, note that

$$\mathsf{E}_c - \mathsf{E}_v = \hbar\omega = \mathsf{E}_g + \frac{\hbar^2 k^2}{2m_r^*}$$

so

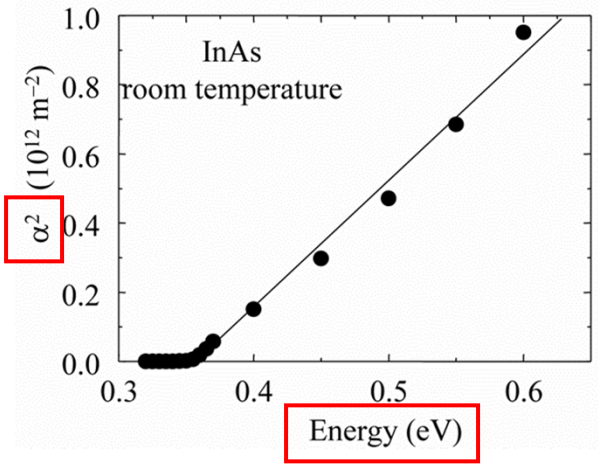
$$k = \left[\frac{2m_r^*}{\hbar^2}(\hbar\omega - \mathsf{E}_g)\right]^{1/2}$$

and finally the joint density of states for a 2 band system with spherical, parabolic bands is

$$\rho_{vc}(\hbar\omega) = \frac{1}{2\pi^2}\left[\frac{2m_r^*}{\hbar^2}\right]^{3/2}(\hbar\omega - \mathsf{E}_g)^{1/2}$$

$$\Gamma = \frac{2\pi}{\hbar}|H'_{vc}|^2 \rho_{vc}(E_c(k) - E_v(k) - \hbar\omega)$$

InAs band edge absorption



InAs is a direct gap III–V semiconductor with $E_g = 0.35$ eV

$h\nu < E_g$: $\alpha = 0$

$h\nu > E_g$:
$\alpha \propto (h\nu - E_g)^{1/2}$

Fermi's Golden Rule:

Spontaneous emission rate $\Gamma(\omega) = \frac{2\pi}{\hbar}\left\langle |M|^2 \right\rangle \rho(\omega_{if})$

$\rho(\omega)$ Density of states

M: transition matrix elements

$$M_{if} = \int \psi_i V \psi_f \, dv$$

Operator for the physical interaction that couples the initial and final states

Selection Rule: Electric Dipole (E1) Transition

Light interaction with dipole moment (p=ex): $H = E\vec{p} = eE\vec{x}$

Light as harmonic EM plane wave

$$E(x,t) = E_0 e^{i(kx-\omega t)}$$

In general, the wavelength of the type of electromagnetic radiation which induces, or is emitted during, transitions between different atomic energy levels is much larger than the typical size of an atom.

$$x << \lambda \Rightarrow kx = \frac{2\pi}{\lambda} x \approx 0$$

Electric dipole approximation $e^{ikx} \approx 1$

Transition dipole moment $H^P_{mn}(0) = eE\int_V \Psi_m \vec{x} \Psi_n dV$

$$M_{12} \propto \int \psi_1 x \psi_2 d^3r$$
$$M_{12} \propto \int \psi_1 y \psi_2 d^3r$$
$$M_{12} \propto \int \psi_1 z \psi_2 d^3r$$

For x, y, z polarized light

$$\Gamma(\omega) = \frac{2\pi}{\hbar}\left\langle |M|^2 \right\rangle \rho(\omega)$$

Selection Rule: Electric Dipole (E1) Transition

Dipole Moment

$$M_{12} \propto \int \psi_1 x \psi_2 d^3r$$
$$M_{12} \propto \int \psi_1 y \psi_2 d^3r$$
$$M_{12} \propto \int \psi_1 z \psi_2 d^3r$$

Matrix element (dipole moment) is non-zero → allowed electric dipole transition

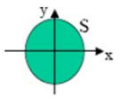
Parity of wavefunction: sign change under inversion about the origin
even parity: f(-x)=f(x)
odd parity: f(-x)=-f(x)

→Initial/final wavefunctions must have different parities for allowed electric dipole transition!

Electronic Transitions in H atoms

Hydrogen atom: lowest state 1S, optical transition between 1S & 2S?

Both states are symmetric, angular momentum l=0



$$\psi_{1S}(-x) = \psi_{1S}(x)$$

$$\psi_{2S}(-x) = \psi_{2S}(x)$$

$$H'_{21}(0) = \int_{-\infty}^{\infty} \psi_2 \vec{x} \psi_1 \, dv$$

$$= \int_0^{\infty} \psi_2(x) \vec{x} \psi_1(x) dv + \int_0^{\infty} \psi_2(-x)(-\vec{x}) \psi_1(-x) dv$$

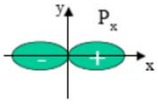
$$= 0$$

No electronic transition between 1S and 2S!

Electronic Transitions in H atoms

Hydrogen atom: lowest state 1S, optical transition between 1S & 2P?

2P is asymmetric, angular momentum l=1



$$\psi_{2p}(-x) = -\psi_{2p}(x)$$

$$H'_{21}(0) = \int_0^{\infty} \psi_2(x) \vec{x} \psi_1(x) dv$$

$$+ \int_0^{\infty} \psi_2(-x)(-\vec{x}) \psi_1(-x) dv$$

$$\neq 0$$

Electronic transition between 1S and 2P is allowed!

Selection Rules

Symmetric function (gerade): $\Psi(-x) = \Psi(x)$

Asymmetric function (ungerade): $\Psi(-x) = -\Psi(x)$

The operator of the electric field: -(x)=-x

Transition between two gerade functions:

$$H_{21}^{p}(0) = \int_{-\infty}^{\infty} gugdV = \int_{-\infty}^{\infty} udV = 0$$ **Forbidden**

Transition between gerade and ungerade functions:

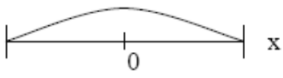
$$H_{21}^{p}(0) = \int_{-\infty}^{\infty} uugdV = \int_{-\infty}^{\infty} gdV \neq 0$$ **Allowed**

Selection rule for electronic transition: $\Delta l = \pm 1$

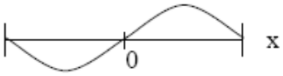
Chem 253, UC, Berkeley

Electronic Transitions: Particle in a box

ground state: g-symmetry $\Psi_0^0(-x) = \Psi_0^0(x)$

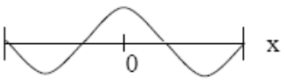


1st exited state: u-symmetry $\Psi_1^0(-x) = -\Psi_1^0(x)$



=> optical transition between ground and 1st excited state is allowed

2nd exited state: g-symmetry $\Psi_2^0(-x) = \Psi_2^0(x)$



=> optical transition between ground and 2nd excited state is forbidden

$\Rightarrow$ selection rule $\Delta n = \pm 1$