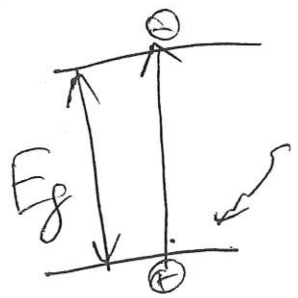
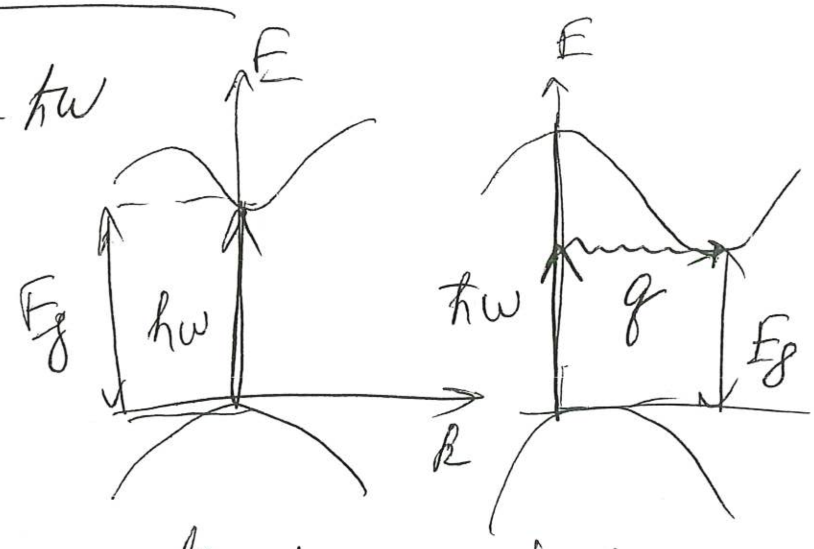
Interband transitions



$$E_f = E_i + \hbar\omega$$



direct   indirect

Direct absorption

Recall: transition rate from QM $W_{i\to f} = \frac{2\pi}{\hbar} |M|^2 g(\hbar\omega)$

matrix element

density of states

pairs of states separated by $\hbar\omega$

$$M = \langle f | \underbrace{H'}_{-\vec{p}_e \cdot \vec{\mathcal{E}}_{photon}} | i \rangle = \int \psi_f^* H' \psi_i \, d\vec{r}$$

light field

electric dipole moment

$$\vec{\mathcal{E}}_{photon} = \vec{\mathcal{E}}_0 e^{i\vec{k}\cdot\vec{r}} \Rightarrow H' = e\vec{\mathcal{E}}_0 \cdot \vec{r} e^{i\vec{k}\cdot\vec{r}}$$

$$\psi_{i,f}(\vec{r}) = \frac{1}{\sqrt{V}} u_{i,f}(\vec{r}) e^{i\vec{k}_{i,f}\cdot\vec{r}}$$

$$M = \frac{e}{V} \int u_f^*(\vec{r}) e^{-i\vec{k}_f\cdot\vec{r}} \left(\vec{\mathcal{E}}_0 \cdot \vec{r} e^{i\vec{k}\cdot\vec{r}}\right) u_i(\vec{r}) e^{i\vec{k}_i\cdot\vec{r}} d\vec{r}$$

- $\hbar\vec{k}_f - \hbar\vec{k}_i = \hbar\vec{k}$ ← conservation of momentum

- u_i, u_f are periodic functions with periodicity of the lattice ⇒ separate the integral over the whole crystal into a sum over identical unit cells

⇓

$$|M| \sim \int_{\text{unit cell}} u_i^*(\vec{r}) \times u_f(\vec{r})\, d^3\vec{r}$$

derived from atomic orbitals of the constituent atoms

assume $\vec{\mathcal{E}} \parallel Ox$

Note: $\frac{2\pi}{\lambda} \sim 10^7\ m^{-1}$ (optical range) $\quad \frac{\pi}{a} \sim 10^{10}\ m^{-1} \gg \frac{2\pi}{\lambda}$ ⇒ neglect photon momentum ($a \sim 10^{-10}\ m$)

$\vec{K}_f \simeq \vec{K}_i$ ⇐ vertical transitions

Now $g(\hbar\omega)$:
joint density of states at photon energy ⇒ accounts for the fact that both initial & final electron states lie within continuous bands

$$g(E)\,dE = 2\,g(K)\,dK \Rightarrow g(E) = \frac{2g(K)}{dE/dK}$$

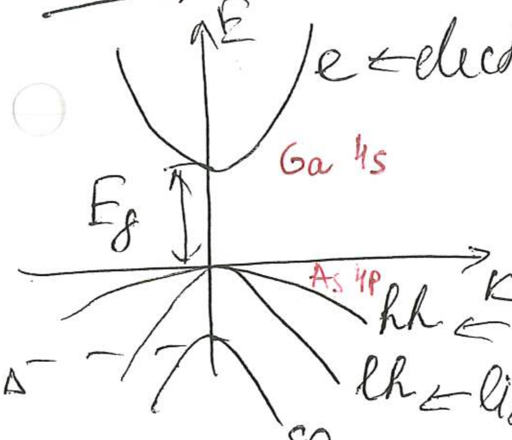
(2: spin)

$$g(K)\,dK = \frac{1}{(2\pi)^3}\, 4\pi K^2\, dK \Rightarrow g(K) = \frac{K^2}{2\pi^2} \Rightarrow$$

$$g(E) = \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2} E^{1/2}$$

← evaluate at E_i & E_f when they are related to $\hbar\omega$ through the band energies

Example direct gap III–V GaAs



e ← electron

hh ← heavy hole → higher DOS → dominates conduction

lh ← light hole

so ← split-off hole

$j=\frac{3}{2}, m_j=\pm\frac{3}{2}$

$j=\frac{3}{2}, m_j=\pm\frac{1}{2}$

$j=\frac{1}{2}$

$$E_c(k)=E_g+\frac{\hbar^2k^2}{2m_e^*}$$

$$E_{hh}(k)=-\frac{\hbar^2k^2}{2m_{hh}^*}$$

$$E_{lh}(k)=-\frac{\hbar^2k^2}{2m_{lh}^*}$$

$$E_{so}(k)=-\Delta-\frac{\hbar^2k^2}{2m_{so}^*}$$

Δ: 0.34 eV ← spin-orbit energy

Energy conservation:

$$\hbar\omega=E_g+\frac{\hbar^2k^2}{2m_e^*}+\frac{\hbar^2k^2}{2m_h^*}=E_g+\frac{\hbar^2k^2}{2\mu}$$

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

$$g(\hbar\omega)=0 \text{ for } \hbar\omega<E_g$$

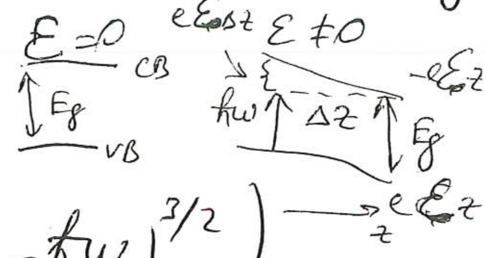
$$g(\hbar\omega)=\frac{1}{2\pi^2}\left(\frac{2\mu}{\hbar^2}\right)^{3/2}(\hbar\omega-E_g)^{1/2} \text{ for } \hbar\omega\geq E_g$$

So, absorption coefficient $\alpha(\hbar\omega)=0$ at $\hbar\omega<E_g$

$\alpha(\hbar\omega)\sim(\hbar\omega-E_g)^{1/2}$ at $\hbar\omega>E_g$

Also, larger $\mu \Rightarrow$ stronger α

The Franz-Keldysh effect (1958)



- $\alpha(\hbar\omega)\sim\exp\left(-\frac{4\sqrt{2m_e^*}}{3|e|\hbar\mathcal{E}}(E_g-\hbar\omega)^{3/2}\right)$ ← applied electric field

band edge shifts to lower energies

- for $\hbar\omega>E_g$, α is modified by an oscillatory function

Recall: (H)-atom in magnetic fields

$\uparrow \vec{B} \parallel Oz$ $\quad \hat{H} = \frac{1}{2m}\left(\hat{\vec{p}} - \frac{q\hat{\vec{A}}}{c}\right)^2 + V$ ← Coulomb

$\vec{B} = \vec{\nabla} \times \vec{A} \Rightarrow \hat{\vec{A}} = \begin{pmatrix} 0 \\ Bx \\ 0 \end{pmatrix} \Rightarrow \hat{H} = \frac{\hat{p}_x^2}{2m} + \frac{1}{2m}\left(\hat{p}_y - \frac{qBx}{c}\right)^2$

strong magnetic fields ⇓ neglect V

$[\hat{p}_y, \hat{H}] = 0$

⇓

$\hat{p}_y \Rightarrow \hbar k_y$

⇓

$$\hat{H} = \frac{\hat{p}_x^2}{2m} + \frac{1}{2} m \omega_c^2 \left(x - \frac{\hbar k_y}{m\omega_c}\right)^2 \Rightarrow \text{harmonic oscillator}$$

$\omega_c = \frac{qB}{mc}$

(equilibrium shifted by $x_0 = \frac{\hbar k_y}{m\omega_c}$)

⇓

$E_n = \hbar\omega_c\left(n + \frac{1}{2}\right)$ ⇒ Observed if $kT \ll \hbar\omega_c$

$$\Psi(x,y) = \underbrace{e^{ik_y y}}_{\text{momentum eigenstates}} \underbrace{\varphi_n(x - x_0)}_{\text{H.O eigenstates}}$$

← F.-K. effect hole

· Typically observed when the semicond. is incorporated as a thin i-region at the p-n junction.

Band edge absorption in a magnetic field

Recall: $\omega_c = \frac{eB}{m_0}$; $E_n = \hbar\omega_c\left(n+\frac{1}{2}\right)$ ← Landau levels

↑ cyclotron frequency

Strong magnetic field along z ⇒ motion of e^- in the conduction band and h^+ in the valence band quantized in the x-y plane, but free along z

⇙

$$E^n(K_z) = \frac{e\hbar B}{m^*}\left(n+\frac{1}{2}\right) + \frac{\hbar^2 K_z^2}{2m^*} \Rightarrow$$

$$E_n^e(K_z) = E_g + \left(n+\frac{1}{2}\right)\frac{e\hbar B}{m_e^*} + \frac{\hbar^2 K_z^2}{2m_e^*}$$

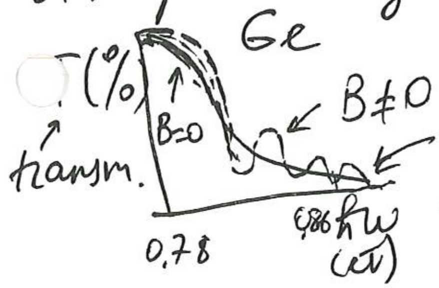
$$E_n^h(K_z) = -\left(n+\frac{1}{2}\right)\frac{e\hbar B}{m_h^*} - \frac{\hbar^2 K_z^2}{2m_h^*}$$

Now shine light ⇒ $\hbar\omega = E_n^e(K_z) - E_n^h(K_z) = E_g + \left(n+\frac{1}{2}\right)\frac{e\hbar B}{\mu} + \frac{\hbar^2 K_z^2}{2\mu}$

↑ selection rule $\Delta n = 0$ ↖ e^- & h^+ have same n

⇓

high absorption at any photon energy that satisfies ⇒ series of equally spaced peaks in the abs. spectrum with energies given by $\hbar\omega = E_g + \left(n+\frac{1}{2}\right)\frac{e\hbar B}{\mu}$, $n = 0, 1, 2, \ldots$ ⇒ absorption edge shift to higher energy by $\frac{\hbar e B}{2\mu}$ ⇒



· width of the dips is determined by line broaden. due to scattering

· energies of the minima ⇒ get m_e^* or μ

Band edge absorption in indirect gap semicond.

Consider an indirect transition $(E_i, \vec{K}_i) \Rightarrow (E_f, \vec{K}_f)$

valence band ↑ ↑ conduction band

Energy conservation:

$$E_f = E_i + \underbrace{\hbar\omega}_{\text{photon energy}} \pm \underbrace{\hbar\Omega}_{\text{phonon energy}}$$

abs.

emission

Momentum conservation: $\hbar\vec{K}_f = \hbar\vec{K}_i \pm \hbar\vec{q}$ ← neglect photon momentum

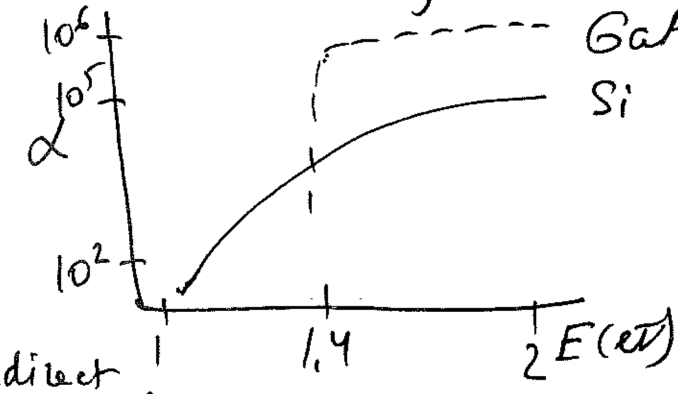
Indirect transitions: photons & phonons are involved ⇒ QM ⇒ 2nd order process: a photon must be destroyed, and a phonon must be either created or destroyed

Direct transitions:

1st order processes (no phonons involved) ⟹

transition rate $W_{i\to f}$ for direct absorption >> indirect absorption

Ex.:

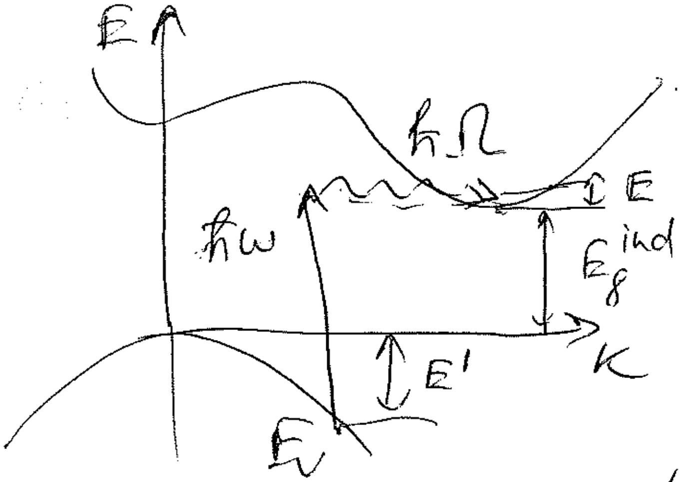


compare to $(\hbar\omega - E_g)^{1/2}$ for direct!

$$\alpha^{\text{indirect}}(\hbar\omega) \sim (\hbar\omega - E_g \mp \hbar\Omega)^2$$

← threshold is at $E_g \mp \hbar\Omega$ depending on whether the phonon is absorbed or emitted

Consider indirect transition $\Rightarrow$



$$E_c = E_g^{ind} + E$$

$$E_v = -E'$$

$$\underbrace{E_v}_{\overset{\shortparallel}{-E'}} + \hbar\omega \underset{\text{em.}}{\overset{\text{abs.}}{\pm}} \hbar\Omega = \underbrace{E_c}_{\overset{\shortparallel}{E_g^{ind} + E}}$$

$$E = \hbar\omega - E_g^{ind} - E' \pm \hbar\Omega \qquad E'_{max} = \hbar\omega - E_g^{ind} \pm \hbar\Omega$$

For a fixed E', the number of states in dE is

$$g_c(E) = \frac{1}{2\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2} E^{1/2} = \frac{1}{2\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2} \cdot (\hbar\omega - E_g^{ind} - E' \pm \hbar\Omega)^{1/2}$$

DOS $N_{3D}(E)$

To obtain joint density of states:

$$g(E) = \underbrace{\frac{1}{2\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2} \cdot \frac{1}{2\pi^2}\left(\frac{2m_h^*}{\hbar^2}\right)^{3/2}}_{C} \int_0^{E'_{max}} dE' \, (\hbar\omega - E_g^{ind} - E' \pm \hbar\Omega)^{1/2} \cdot E'^{1/2} = C \underbrace{\int_0^{E'_{max}} dE' \, (E'_{max} - E')^{1/2} E'^{1/2}}_{} = C \frac{\pi}{8} E'^2_{max}$$

$$E'_{max} = \hbar\omega - E_g^{ind} \pm \hbar\Omega \qquad \frac{\pi}{8} E'^2_{max} \text{ for } E'_{max} > 0$$

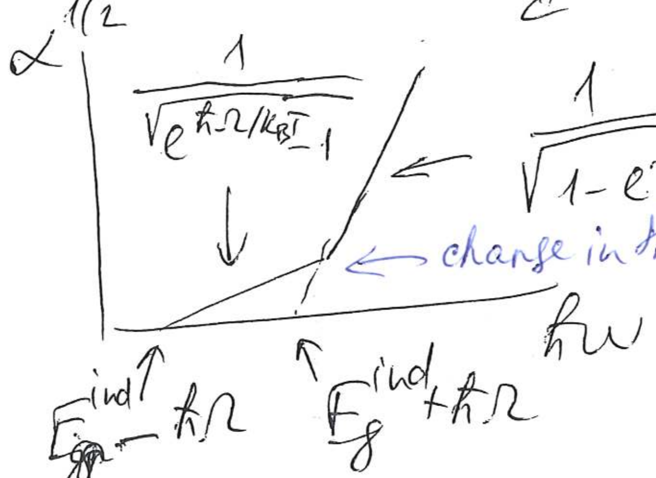
So, $g(E) = C \dfrac{\pi}{8} (\hbar\omega - E_g^{ind} \pm \hbar\Omega)^2$ if $\hbar\omega > E_g^{ind} \pm \hbar\Omega$

joint DOS $\quad \alpha \sim g(E)$

absorption coeff.

Then, $\alpha_{ph.emission} \sim \dfrac{\left(\hbar\omega - E_g^{ind} - \hbar\Omega\right)^2}{1 - e^{-\hbar\Omega/k_BT}}$

So, $\alpha^{1/2}$ should be linear with $\hbar\omega$



$$\Leftarrow \quad \frac{1}{\sqrt{1-e^{-\hbar\Omega/k_BT}}} + \frac{1}{\sqrt{e^{\hbar\Omega/k_BT}-1}}$$

← change in the slope when phonon absorption kicks in

$$\text{Total } \alpha_{indirect} = \tilde{C}\left\{ \frac{\left(\hbar\omega - E_g^{ind} + \hbar\Omega\right)^2}{e^{\hbar\Omega/k_BT}-1} + \frac{\left(\hbar\omega - E_g^{ind} - \hbar\Omega\right)^2}{1-e^{-\hbar\Omega/k_BT}} \right\} \text{ for } \hbar\omega \geq E_g^{ind} \pm \hbar\Omega$$

Low temperatures $\Rightarrow k_BT \ll \hbar\Omega \Rightarrow \dfrac{1}{e^{\hbar\Omega/k_BT}-1} \approx e^{-\frac{\hbar\Omega}{k_BT}}$

$\Downarrow$

phonon absorption term is strongly suppressed

$\dfrac{1}{1-e^{-\hbar\Omega/k_BT}} \approx 1 \Leftarrow$ phonon emission dominates

Temperature dependence of absorption edge

direct bandgap $\Rightarrow$ $\alpha(T) \sim (\hbar\omega - E_g(T))^{1/2}$

$$E_g = E_g^0 + \left(\frac{\partial E_g}{\partial T}\right)_p \Delta T + \left(\frac{\partial E_g}{\partial p}\right)_T \Delta p$$

p ← pressure

	$\partial E_g / \partial T$
Si	$-2.3 \cdot 10^{-4}\ \frac{eV}{K}$
Ge	$-3.7 \cdot 10^{-4}$
GaAs	$-5 \cdot 10^{-4}$
HgTe	$5.6 \cdot 10^{-4}\ \frac{eV}{K}$

indirect bandgap $\Rightarrow$ take into account phonon population factors!

phonon absorption $\Rightarrow$ $\underbrace{|n_K\rangle}_{\text{initial state}} \Rightarrow \underbrace{|n_K - 1\rangle}_{\text{final state}}$

transition operator $\Rightarrow$ matrix element $|M|^2 \Rightarrow$
must involve a ← phonon annihilation operator

$$\sim |\langle n_K - 1 | a | n_K\rangle|^2 = |\langle n_K - 1 | \sqrt{n_K} | n_K - 1\rangle|^2 = n_K$$

phonon population

$$n_K = \frac{1}{e^{\hbar\Omega/k_B T} - 1}$$

follows Bose-Einstein statistics

So
$$\alpha_{ph.abs.} \sim \frac{(\hbar\omega - E_g^{ind} + \hbar\Omega)^2}{e^{\hbar\Omega/k_B T} - 1}$$

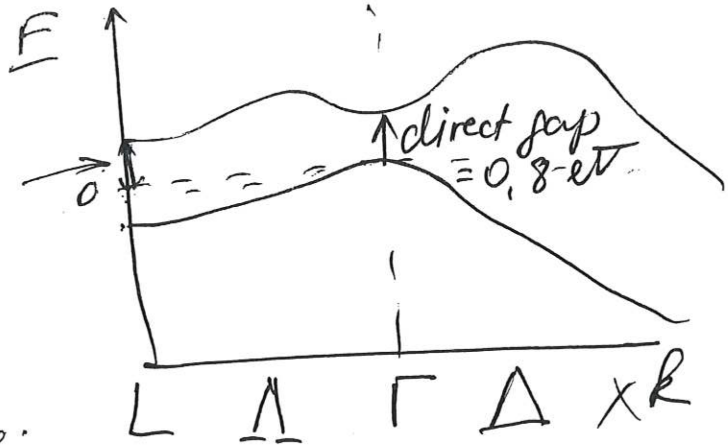
phonon emission $\Rightarrow$ $|n_K + 1\rangle$ final state $\Rightarrow |\langle n_K + 1 | a^+ | n_K\rangle|^2$

$$= n_K + 1 = \frac{1}{e^{\hbar\Omega/k_B T} - 1} + 1 = \frac{1}{1 - e^{-\hbar\Omega/k_B T}}$$

Ex. Ge

$0.66\,eV =$ indirect gap at L point

$\vec{k} = \frac{\pi}{a}(1,1,1)$



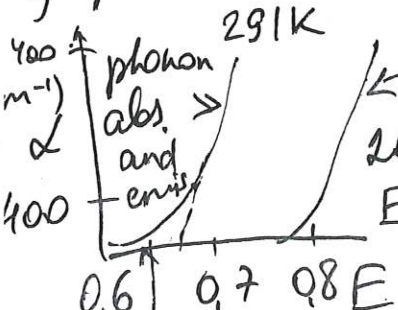
Indirect absorption edge:

$\alpha \sim (\hbar\omega - E_g \mp \hbar\Omega)^2$ ← in general, expect contributions both from phonon emission & absorption

Phonon emission is possible at all $t°$; phonon abs. - only if phonons are thermally excited $\Rightarrow f_{BE}(\hbar\Omega) = \frac{1}{e^{\hbar\Omega/k_BT} - 1}$

phonons with $\Omega \sim f_{BE}$

since the # particles doesn't have to be conserved → $\mu = 0$ ← chem. potential



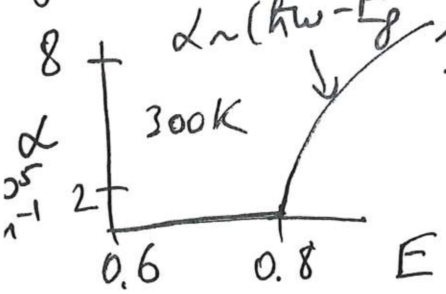
tail can extend

$E_g + \hbar\Omega = 0.76\,eV$

band gap of Ge @ 20K is $0.74\,eV \Rightarrow$ phonon energy is $0.02\,eV$

far as it is possible to absorb more than 1 phonon

$\alpha \sim (\hbar\omega - E_g^{dir})^{1/2}$ ← much sharper than indirect

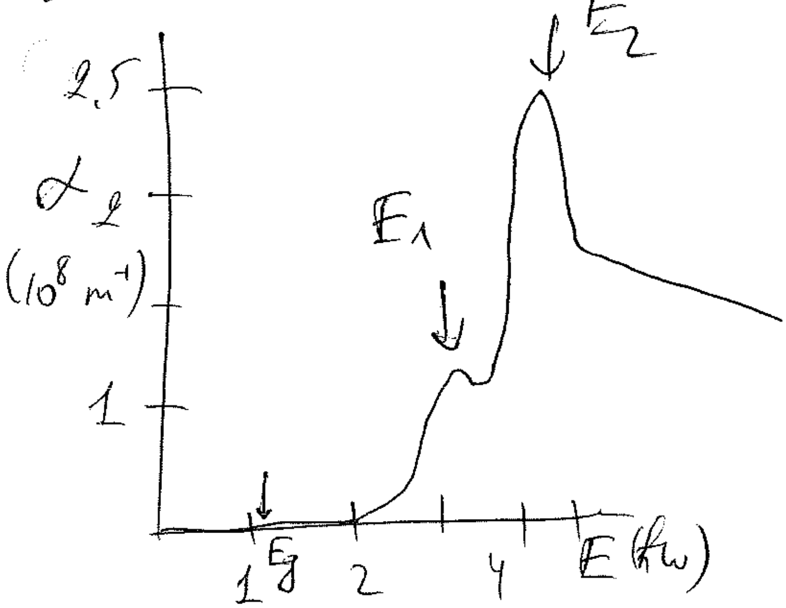


Phys Rev (1955)

Note: 2D: $\alpha \sim (E - E_g \pm \hbar\Omega)$

1D: $\alpha \sim (E - E_g \pm \hbar\Omega)^{1/2}$

Interband absorption above the band edge



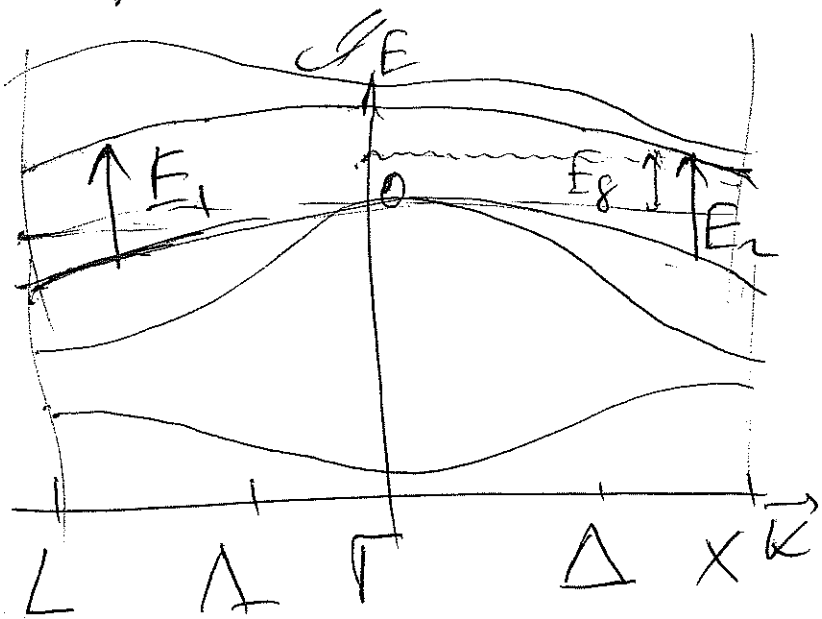
measured abs. spectrum is dominated by direct absorption at $\hbar\omega$ where DOS is high

<u>Recall;</u>

$$g(E)\,dE = 2\,g(k)\,dk \quad (2 = \text{spin})$$

$$g(E) = \frac{2\,g(k)}{dE/dk}, \qquad g(k) = \frac{1}{(2\pi)^3}4\pi k^2$$

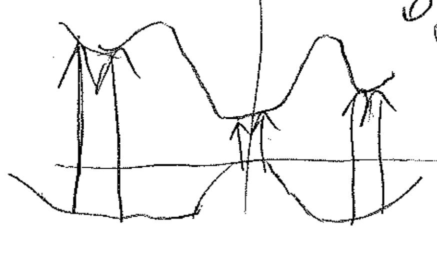
$g(E)$ is high if $\frac{dE}{dk}$ is low; since $\alpha \sim g(E)$ (joint DOS) $\Rightarrow$ the largest absorption between bands which are parallel and flat



$$\vec{\nabla}_k\left(E_v(\vec{k}) - E_c(\vec{k})\right) = 0$$

$\Downarrow$

insert into $g(E)$ instead of $\frac{dE}{dk}$ for 3D version of JDOS



← enhanced absorption here