# Lecture 3 – 24/09/2025

## Effective mass approximation

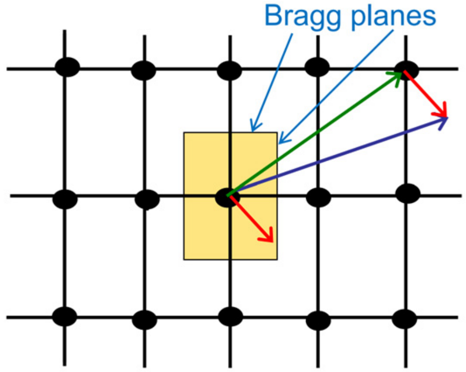
- Electrons
- Holes
- Valence band structure in cubic and hexagonal semiconductors

# Summary Lecture 2

- **Reciprocal space** : Wave vectors with plane waves with the periodicity of the lattice

$$\mathbf{b_i}\cdot\mathbf{a_j} = 2\pi\delta_{ij}$$

- **1st Brillouin zone** : region about a point lattice closer to that point then any other lattice point



- **Bloch Functions**

$$H_e\psi_n(\mathbf{r}) = \left(\frac{p^2}{2m}+V(\mathbf{r})\right)\psi_n(\mathbf{r}) = E_n\psi_n(\mathbf{r})$$

with $V(\mathrm{r})$ which is periodic: $V(\mathbf{r}+\mathbf{T}) = V(\mathbf{r})$

$$\boxed{\psi_n(\mathbf{r}) = \boxed{u_{n,k}(\mathbf{r})}\boxed{e^{i\mathbf{k}.\mathbf{r}}}}$$

- **Energy of electrons :** $E_n(\mathrm{k})$, symmetry

# Summary Lecture 2

- **Nearly free electron model** : Potential *V* periodic small compared kinetic energy

$$H = -\frac{\hbar^2}{2m_0}\nabla^2 + V(x) \xrightarrow{(1)\ \&\ (2)} \boxed{\left(\frac{\hbar^2 k^2}{2m_0} - E_k\right)C(k) + \sum_G V_G C(k-G) = 0}$$

(1) : Fourier series from periodic potential

$$V(x) = \sum_G V_G\, e^{iGx}$$

(2) : Born – von Karman boundary conditions

$$\psi(x) = \sum_K C(K)\, e^{-iKx}$$

- **Particular case** : *k* near edge 1st Brillouin zone ⇒ *k* = *G*/2 and one Fourier component dominates

$$\begin{bmatrix} \frac{\hbar^2 G^2}{8m_0} - E & V \\ V & \frac{\hbar^2 G^2}{8m_0} - E \end{bmatrix} \Longrightarrow \boxed{E_\pm = E_0 \pm V + \frac{\hbar^2 q^2}{2m_0}\left(1 \pm \frac{2E_0}{V}\right)}$$

$q = k - G/2$

$$E_0 = \hbar^2 G^2 / 8m_0$$

- **Effective mass** $E_+ = E_0^+ + \frac{\hbar^2 q^2}{2m_+^*}$ $E_- = E_0^- + \frac{\hbar^2 q^2}{2m_-^*}$

$$\boxed{m_\pm^* = \hbar^2 \left(\frac{\mathrm{d}^2 E}{\mathrm{d}q^2}\right)^{-1} = m_0 \frac{1}{1 \pm \frac{2E_0}{V}} \approx \pm m_0 \frac{V}{2E_0}}$$

# *k.p* method

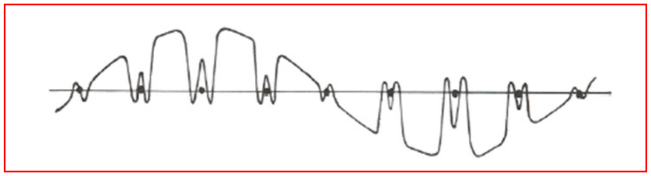
**Previous approach** (nearly-free electron model) ⇒ leads to the formation of forbidden energy band(s) but it remains difficult to predict the exact value of the bandgap or that of the effective masses

***k.p* method**: semi-empirical method relying on numbers deduced from experiments

# *k.p* method

Overview

$$\left[\frac{\mathbf{p}^2}{2m_0}+V(\mathbf{r})\right]\psi_{n,\mathbf{k}}(\mathbf{r})=E_{n,\mathbf{k}}(\mathbf{r})\psi_{n,\mathbf{k}}(\mathbf{r})$$



The eigenfunctions $\psi_{n,\mathbf{k}}(\mathbf{r})$ are Bloch functions, which write as:

$u_{n,\mathbf{k}}(\mathbf{r})e^{i\mathbf{kr}}$ with $u_{n,\mathbf{k}}(\mathbf{r})=u_{n,\mathbf{k}}(\mathbf{r}+\mathbf{T})$ (with $\mathbf{T}$ a vector of the lattice)

One does recall that the operators **p** and **p**$^2$ behave as follows:

$$\mathbf{p}\psi_{n,\mathbf{k}}(\mathbf{r})=e^{i\mathbf{kr}}\left[(\mathbf{p}+\hbar\mathbf{k})u_{n,\mathbf{k}}(\mathbf{r})\right] \quad \text{and } \mathbf{p}=-i\hbar\nabla$$

$$\mathbf{p}^2\psi_{n,\mathbf{k}}(\mathbf{r})=e^{i\mathbf{kr}}\left[(\mathbf{p}+\hbar\mathbf{k})^2u_{n,\mathbf{k}}(\mathbf{r})\right]$$

One can thus rewrite Schrödinger's equation such that:

$$\left[\frac{(\mathbf{p}+\hbar\mathbf{k})^2}{2m_0}+V(\mathbf{r})\right]u_{n,\mathbf{k}}(\mathbf{r})=E_{n,\mathbf{k}}u_{n,\mathbf{k}}(\mathbf{r})$$

$$\left[\frac{\mathbf{p}^2}{2m_0}+\boxed{\frac{\hbar\mathbf{k}\cdot\mathbf{p}}{m_0}}+\frac{\hbar^2\mathbf{k}^2}{2m_0}+V(\mathbf{r})\right]u_{n,\mathbf{k}}(\mathbf{r})=E_{n,\mathbf{k}}u_{n,\mathbf{k}}(\mathbf{r})$$

# *k.p* method

Overview

At $k \approx 0$, $\hbar \mathbf{k}.\mathbf{p}/m_0$ can be considered as a perturbation

⇒ The eigenenergies are then given by:

$$E_{n,\mathbf{k}} = E_{n,0} + \frac{\hbar^2 k^2}{2\,m_0} + \frac{\hbar^2}{m_0^2} \sum_{n' \neq n} \frac{\left| \left\langle u_{n',0} \middle| \mathbf{k}.\mathbf{p} \middle| u_{n,0} \right\rangle \right|^2}{E_{n,0} - E_{n',0}}$$

We only pay attention to electronic states close in energy located at the top of the VB and at the bottom of the CB

The energy dispersion of the CB level -in the isotropic case, e.g., for direct bandgap SCs- writes as:

$$E_{\mathrm{c},\mathbf{k}} = E_{\mathrm{c},0} + \frac{\hbar^2 k^2}{2m_0} + \frac{\hbar^2 k^2}{m_0^2} \frac{\left| \left\langle u_{\mathrm{v},0} \middle| p_x \middle| u_{\mathrm{c},0} \right\rangle \right|^2}{E_{\mathrm{c},0} - E_{\mathrm{v},0}}$$

2-band modeling (most simplified treatment) ⇒ topmost states of VB more complex (HH, LH and SO subbands)

$$E_{\mathrm{c},\mathbf{k}} = E_{\mathrm{c},0} + \frac{\hbar^2 k^2}{2m_0} + \frac{\hbar^2 k^2}{2m_0} \frac{P^2}{E_\mathrm{g}} = E_{\mathrm{c},0} + \frac{\hbar^2 k^2}{2m_0} \left( 1 + \frac{P^2}{E_\mathrm{g}} \right)$$

with $P^2 = \frac{2}{m_0} \left| \left\langle u_{\mathrm{v},0} \middle| p_x \middle| u_{\mathrm{c},0} \right\rangle \right|^2$ ≡ energy

*Kane matrix element*

⇒ describes coupling between electronic states in ≠ bands

# *k.p* method

Overview

$$\boxed{E_{\mathrm{c},\mathbf{k}} = E_{\mathrm{c},0} + \frac{\hbar^2 k^2}{2m_0}\left(1 + \frac{P^2}{E_\mathrm{g}}\right) = E_{\mathrm{c},0} + \frac{\hbar^2 k^2}{2m^*}}$$

with $\boxed{m^* = m_0\left(1 + \frac{P^2}{E_\mathrm{g}}\right)^{-1}}$ ***The effective mass varies as the bandgap***

- The matrix element $P^2$ can be deduced from optical properties, e.g., via the measurement of the dielectric function (real + imaginary parts) deduced from spectroscopic ellipsometry or when modeling an interband transition (e.g., oscillator strength such as deduced from absorption or photoluminescence experiments)
- ***$P^2$* is about equal to 20-25 eV for most semiconductors**

$$\boxed{P^2 \approx \frac{2}{m_0}\left(\frac{2\pi\hbar}{a}\right)^2}$$

*Good approximation for zinc-blende semiconductors*

*Relevant literature: See section 2.6 (especially subsection 2.6.1) in the book by Yu & Cardona (cf. Lecture 1)*

# Effective mass: from 2nd Newton’s law

The crystal field affects the electron properties ⇒ different electron mass depending on the material system of interest

2nd Newton’s law of motion: $\mathbf{F} = m^* \frac{d\mathbf{v}}{dt}$

Electrons are described by their Bloch wave function:

$$\psi(\mathbf{r},t) = u(\mathbf{r}) e^{i\mathbf{kr}} e^{-i\omega_k t} \quad \text{with} \quad E_k = \hbar\omega_k$$

The wave packet velocity is given by:

$$\mathbf{v} = \frac{d\omega}{d\mathbf{k}} = \frac{1}{\hbar}\frac{dE}{d\mathbf{k}}$$

and the acceleration writes:

$$\boldsymbol{\gamma} = \frac{d\mathbf{v}}{dt} = \frac{1}{\hbar}\frac{d}{dt}\frac{dE}{d\mathbf{k}} = \frac{1}{\hbar}\frac{d}{d\mathbf{k}}\boxed{\frac{dE}{dt}}$$

# Effective mass

If we apply an external force to an electron, its energy will increase over a certain distance *dx* by:

Infinitesimal work

$$dE = \mathbf{F}d\mathbf{x} = \mathbf{F}\mathbf{v}dt \Rightarrow \frac{dE}{dt} = \mathbf{F}\mathbf{v}$$

Its acceleration is then given by:

$$\boldsymbol{\gamma} = \frac{1}{\hbar}\frac{d}{d\mathbf{k}}\mathbf{F}\mathbf{v} = \mathbf{F}\frac{1}{\hbar}\frac{d}{d\mathbf{k}}\frac{1}{\hbar}\frac{dE}{d\mathbf{k}} = \mathbf{F}\frac{1}{\hbar^2}\frac{d^2E}{d\mathbf{k}^2} \qquad \mathbf{v} = \frac{d\omega}{d\mathbf{k}} = \frac{1}{\hbar}\frac{dE}{d\mathbf{k}}$$

and the effective mass is then defined as:

$$\boxed{m^* = \hbar^2 \Big/ \frac{d^2E}{d\mathbf{k}^2}}$$

# Effective mass

- Inversely proportional to the curvature of the *k*-space energy dispersion
- Effective mass: positive for the CB and negative for the VB (true close to the $\Gamma$ point)
- “Hole” in the VB ⇒ like an electron in the CB. Actually, a hole is a missing electron in the VB!

# Effective mass

- **Direct bandgap** (e.g., GaAs): the CB is isotropic around $k = 0$ ($s$ state)

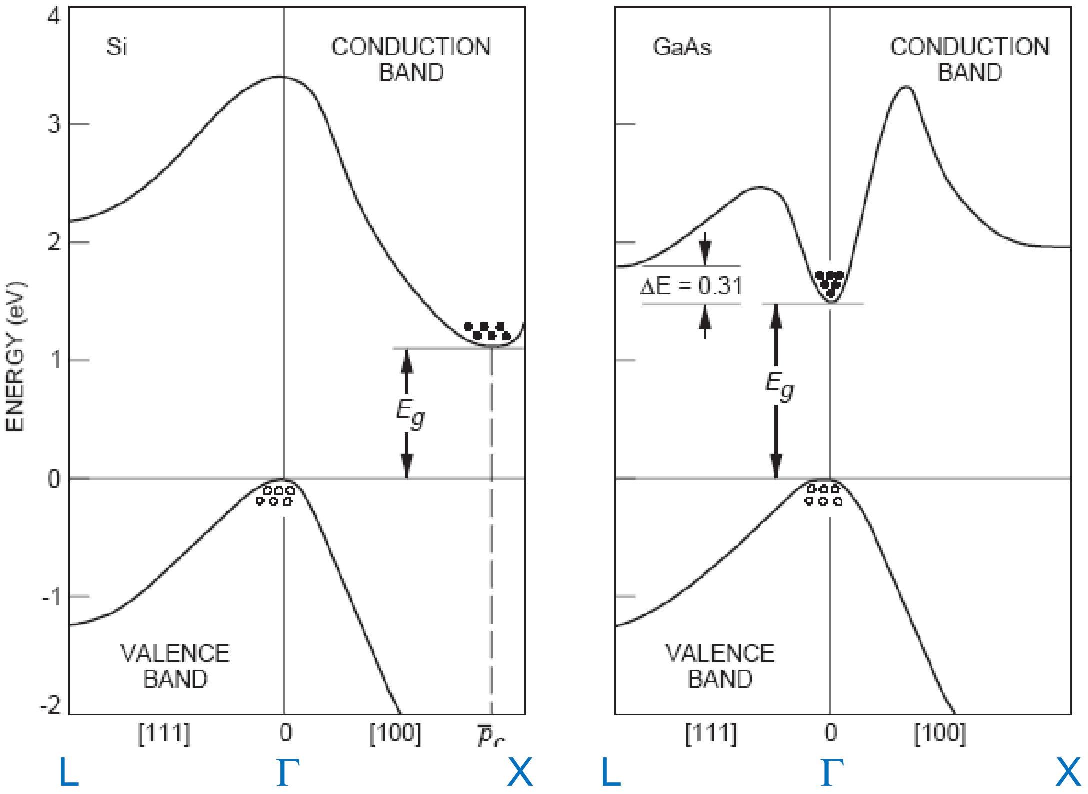
$\Rightarrow$ Isotropic effective mass: the mobility does not depend on the electron motion direction in the crystal

- **Indirect bandgap** (e.g., Si): the CB is anisotropic around the CB energy minimum (different effective masses)

$\Rightarrow$ Energy surface ***E*(*k*) = constant** is **no longer a sphere**, but a series of ellipsoids oriented along the 3 directions of reciprocal space

$$\boxed{E_{\mathrm{C}}(\mathbf{k}) = E_{\mathrm{C}}(0) + \hbar^2\left(\frac{k_1^2}{2m_1} + \frac{k_2^2}{2m_2} + \frac{k_3^2}{2m_3}\right)}$$

# Effective mass



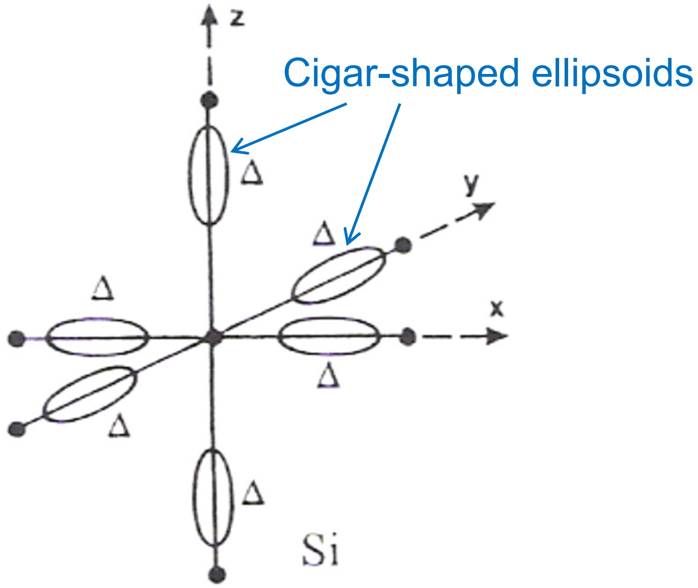
2-band approximation

# Effective mass

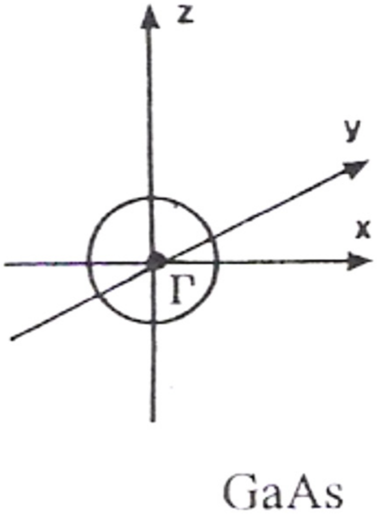
Representation of the constant energy surfaces about the extrema reflecting the effective mass distribution in ***k*-space**

isosurfaces

Reciprocal space representation of isosurfaces



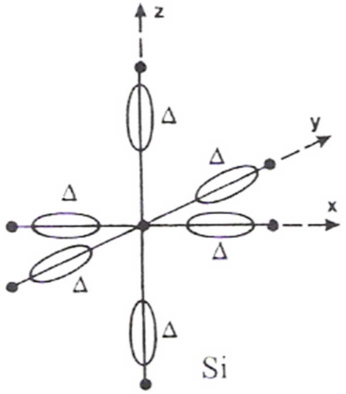
**Anisotropic case**



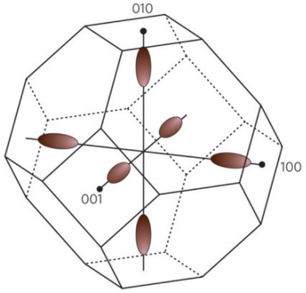
**Isotropic case**

# Effective mass

Si: symmetry-related minima at points
~80% of the way to zone boundary

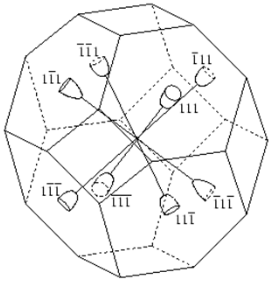


*3-fold symmetry*



**X valleys of Si**

*4-fold symmetry*



**L valleys of Ge**

**Anisotropic case**

Due to cumulative interactions between atomic neighbors, the minimum of the valley in *k*-space may occur not at the $\Gamma$-point (deviation from that of a perfect sphere)

For silicon/germanium, the energy surface for the conduction band consists of six/four ellipsoids of revolution lying along the <100>/<111> directions with a longitudinal mass $m_l$ and a transverse mass $m_t$

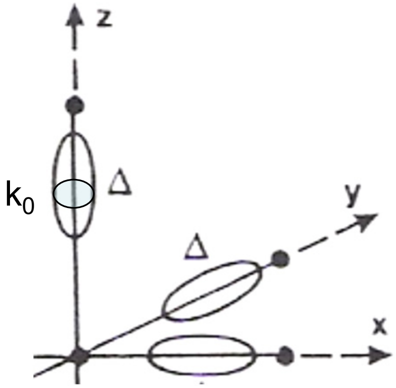
The *average density of states effective mass* is equal to $(6/4 m_l^{1/2} m_t)^{2/3}$

# Effective mass

## Longitudinal and transverse masses

The energy dispersion $E(\mathbf{k})$ can be expanded in Taylor series
About a band extremum $k = k_0$, <u>where the first derivative is zero</u>, $E(\mathbf{k})$ can be expressed as follows:

$$E(\mathbf{k}) = E(\mathbf{k}_0) + \frac{1}{2}\frac{d^2E}{dk_x^2}(k_x - k_{0x})^2 + \frac{1}{2}\frac{d^2E}{dk_y^2}(k_y - k_{0y})^2 + \frac{1}{2}\frac{d^2E}{dk_z^2}(k_z - k_{0z})^2$$



Direct bandgap SC:

$$E_\mathrm{C}(\mathbf{k}) = E_\mathrm{C} + \frac{1}{2}\frac{d^2E}{dk^2}k^2 = E_\mathrm{C} + \frac{\hbar^2 k^2}{2m^*}$$

Indirect bandgap SC: $\left(k_\parallel = k_z, k_\perp = \sqrt{k_x^2 + k_y^2}\right)$

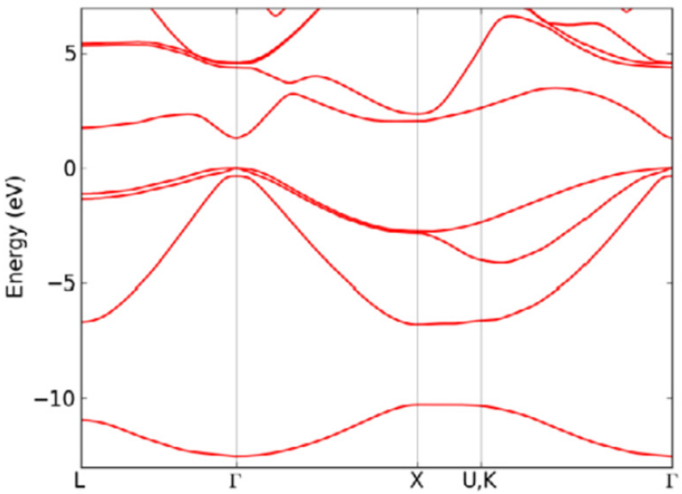
$$E_\mathrm{C}(\mathbf{k}) = E_\mathrm{C} + \frac{1}{2}\frac{d^2E}{dk_\parallel^2}(k_\parallel - k_0)^2 + \frac{1}{2}\frac{d^2E}{dk_\perp^2}k_\perp^2 = E_\mathrm{C} + \boxed{\frac{\hbar^2}{2m_\mathrm{l}^*}(k_\parallel - k_0)^2} + \boxed{\frac{\hbar^2}{2m_\mathrm{t}^*}k_\perp^2}$$

$m_\mathrm{l}$ and $m_\mathrm{t}$ are the longitudinal and transverse effective masses, respectively

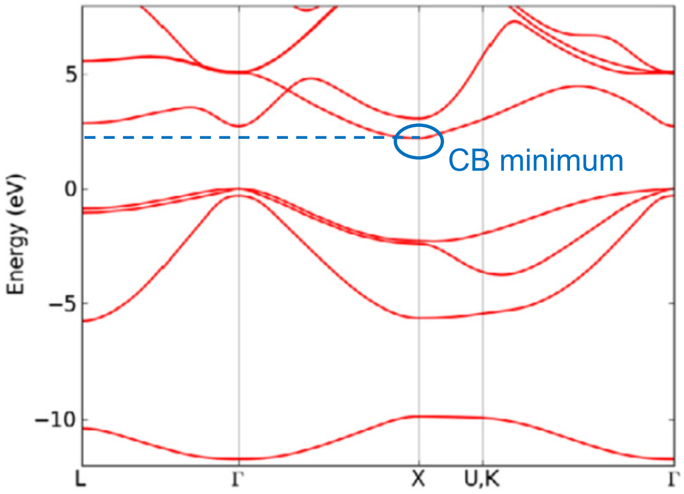
**How can you visualize those two masses on the sketch?**

# Effective mass

**Band structure of GaAs**



**Band structure of AlAs**

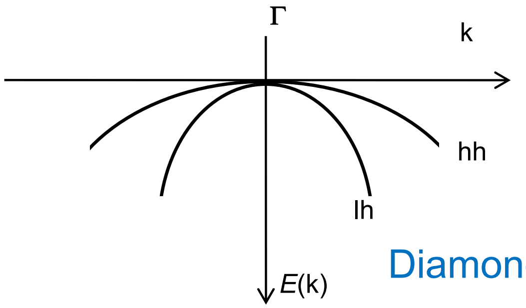


1st principles calculations of quasiparticle band structure

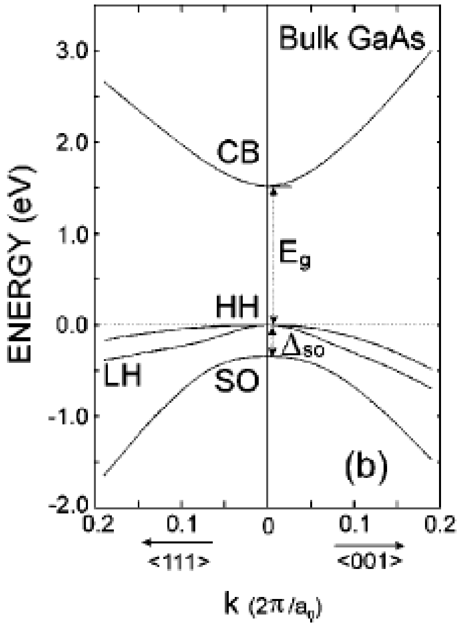
**What will be the effective mass of an electron in the AlGaAs alloy?**

# Effective mass

## Valence band structure:



Diamond and zinc-blende structures



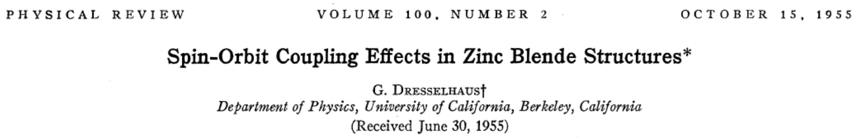
Two branches are degenerate in $k = 0$:

- **Heavy holes (hh)**
- **Light holes (lh)**

**SO band** stands for spin-orbit coupling due to the lack of inversion symmetry in zinc-blende structures (relativistic effect scaling with the atomic number of the atom)

| Compound | AlAs | GaAs | InAs | AlP | GaP | InP | GaN |
|---|---|---|---|---|---|---|---|
| $\Delta_{SO}$ (eV) | 0.28 | 0.341 | 0.39 | 0.07 | 0.08 | 0.108 | 0.017 |

Splitting < $k_B T$ at 300 K!


PHYSICAL REVIEW VOLUME 100, NUMBER 2 OCTOBER 15, 1955

**Spin-Orbit Coupling Effects in Zinc Blende Structures***

G. Dresselhaus†
*Department of Physics, University of California, Berkeley, California*
(Received June 30, 1955)

> 3300 citations!

# Structure of the valence band: Light and heavy holes

Atomic levels are generally degenerate, which may have important consequences for the band energy spectrum of a crystal

**Case of cubic semiconductors (e.g., diamond or zinc-blende SCs) without spin effects**

**p** = **0** CB state is *s*-type ($l = 0$) whereas the corresponding VB state is *p*-type ($l = 1$) and triply degenerate ($m_l = 0, \pm 1$)

$l$: atomic orbital angular momentum
$m_l$: projection of $l$ on an arbitrary axis

Effective mass description of the VB accounting for its threefold degeneracy

≡ band extremum

⇒ Construction of a scalar Hamiltonian invariant under rotations, quadratic in **p**, done using symmetry considerations using **p** and the pseudo-vector of angular momentum **L** (≡ set of 3 × 3 matrices $L_x$, $L_y$, and $L_z$ corresponding to $l = 1$)

Sole possibility, the Luttinger Hamiltonian:

$$\boxed{H = Ap^2\, I + B(\mathbf{pL})^2}$$

where $A$ and $B$ are arbitrary constants, and $I$ is a unit 3 × 3 matrix

# Structure of the valence band: Light and heavy holes

The energy spectrum in the VB is found by diagonalizing the Hamiltonian *H*, e.g., by choosing the direction of the *z*-axis along the vector **p**

$\Rightarrow (\mathbf{pL})^2 = p^2 L_z^2$ and the eigenvalues of *H* are given by:

$$\boxed{E_{\mathrm{hh}}(p) = (A+B)p^2 \text{ for } L_z = \pm 1 \quad \text{and} \quad E_{\mathrm{lh}}(p) = Ap^2 \text{ for } L_z = 0}$$

Thus, the VB energy spectrum has two parabolic branches with the first one, $E_{\mathrm{hh}}(p)$, which is twofold degenerate

Two effective masses can be introduced that follow the relations:

$$\boxed{A+B = \frac{1}{2m_{\mathrm{hh}}} \quad \text{and} \quad A = \frac{1}{2m_{\mathrm{lh}}}}$$

Usually, $B < 0$ but $A + B > 0$

The difference between light and heavy holes is that the heavy hole has a projection of its orbital momentum **L** on the direction of **p** (what is called the *helicity*) equal to ±1 while the light hole has a projection equal to 0

# Effects of spin-orbit interaction on the VB

**The spin-orbit interaction will double all the states but the changes in the energy spectrum will essentially occur at the VB level**

**L** and **S** are no longer conserved separately but only the total angular momentum **J** = **L** + **S** for which the eigenvalues of $J^2$ are $j(j+1)$ with $|l-s| \leq j \leq l+s$

$\Rightarrow$ CB states are not impacted ($j = s = 1/2$) but the VB state with $l = 1$ is split into two states with $j = 3/2$ and $j = 1/2$

For **p** = **0**, we have a fourfold degenerate state ($j = 3/2$ and $J_z = +3/2, +1/2, -1/2, -3/2$) separated by an energy Δ, the *spin-orbit splitting*, from a doubly degenerate state ($j = 1/2$ and $J_z = +1/2, -1/2$)

The CB remains doubly degenerate. The value of Δ is small for materials with light atoms and may be quite large (comparable to $E_g$) in semiconductors composed of heavy atoms like InSb (cf. slide #17 for the trend regarding the magnitude of Δ)

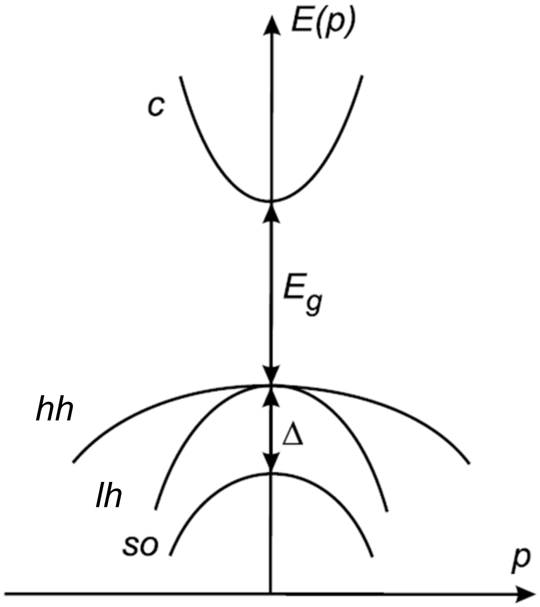
# Effects of spin-orbit interaction on the VB

Regarding the $j$ = 3/2 state for $\mathbf{p} \neq \mathbf{0}$ for energies $E(p) \ll \Delta$, a Luttinger Hamiltonian is constructed in a way similar to the case where SO interaction was neglected. The main difference is that $3 \times 3$ $L_{x,y,z}$ matrices are now replaced by $4 \times 4$ $J_{x,y,z}$ matrices corresponding to $j$ = 3/2

$$\boxed{H = Ap^2\, I + B(\mathbf{pJ})^2}$$

where now $I$ is a unit $4 \times 4$ matrix and the matrix $J_z$ is diagonal with eigenvalues +3/2, +1/2, -1/2, and -3/2

$$\boxed{\begin{aligned} E_{\mathrm{hh}}(p) &= \left(A + \frac{9B}{4}\right)p^2 = \frac{p^2}{2m_{\mathrm{hh}}}\left(J_z = \pm 3/2\right) \\ E_{\mathrm{lh}}(p) &= \left(A + \frac{B}{4}\right)p^2 = \frac{p^2}{2m_{\mathrm{lh}}}\left(J_z = \pm 1/2\right) \end{aligned}}$$



**Band structure of a zinc-blende SC near the Γ-point**

Usually, $B < 0$ but $A + 9B/4 > 0$, hence both masses are > 0

Helicity equal to ±3/2 for HH and ±1/2 for LH

# GaN optical properties (wurtzite structure)

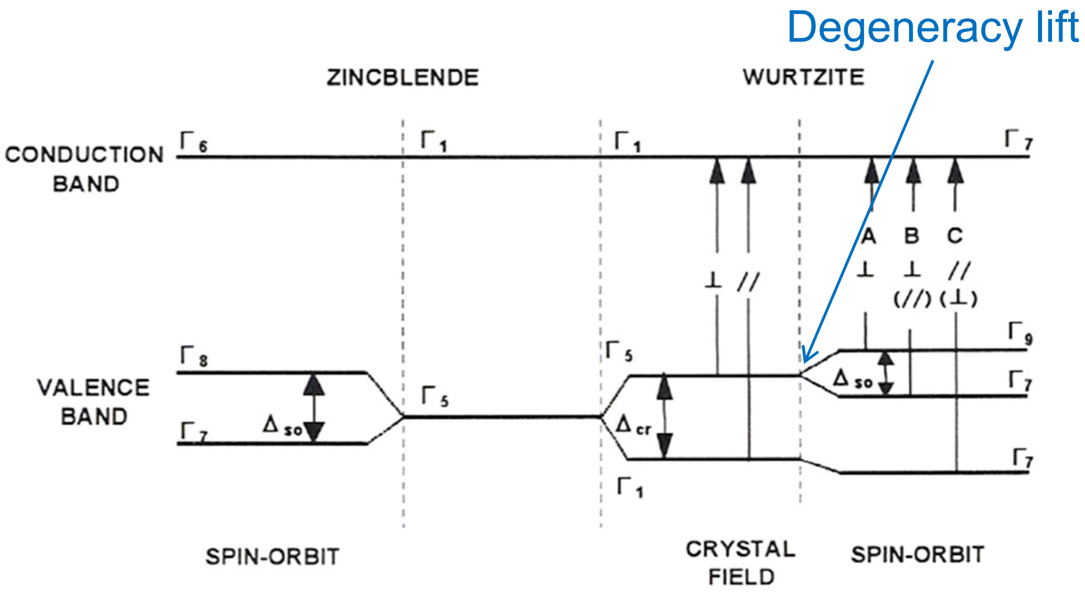
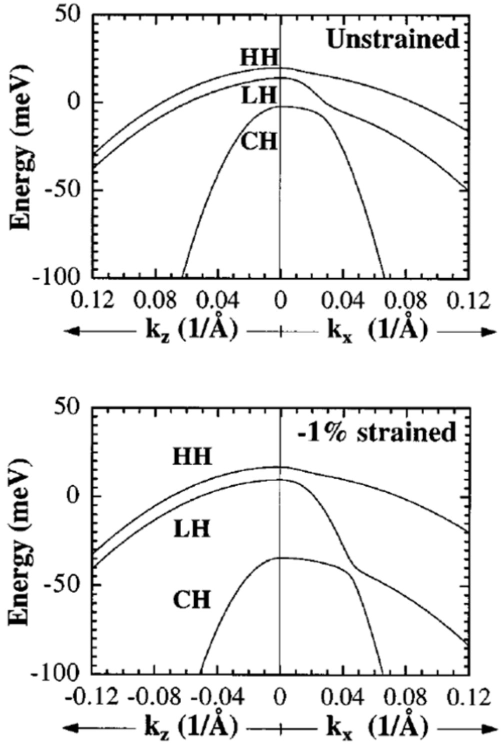

Degeneracy lift

**Figure 5.1** Band structures and labeling of respective transition in zincblende and wurtzite GaN. The indications ⊥ and // show that the transition is allowed for the light polarization $E$ perpendicular and parallel to the optic ($c$) axis, respectively. Parentheses means that the transition is partially allowed. The value $\Delta_{so}$ and $\Delta_{cr}$ are the spin-orbit and crystal-field splittings, respectively.



R. Dingle *et al.*, Phys. Rev. B **4**, 1211 (1971)

S. Nakamura and S. F. Chichibu in “Introduction to nitride semiconductor blue lasers and LEDs” (Taylor & Francis Eds, London, 2000)

# Effective mass

| Semiconductors | Electron effective mass ($m^*/m_0$) | Hole effective mass ($m^*/m_0$) |
|---|---|---|
| Si | 0.92($m_l$)-0.19($m_t$) | 0.53($m_{hh}$)-0.16($m_{lh}$) |
| Ge | 1.59($m_l$)-0.082($m_t$) | 0.35($m_{hh}$)-0.043($m_{lh}$) |
| GaAs | 0.067 | 0.62($m_{hh}$)-0.074($m_{lh}$) |
| InAs | 0.023 | 0.6($m_{hh}$)-0.027($m_{lh}$) |
| GaN | 0.2 | 1.2($m_{hh}$)-0.26($m_{lh}$) |

As will be inferred from carrier statistics, in relaxed (i.e., strain-free) semiconductor layers hole transport will be dominated by heavy holes !

# Band structure of bulk semiconductors - summary

- **Upper level state of the VB in $\Gamma$ (k = 0),**

For cubic SCs, two degenerate bands with different masses $m_{hh} >> m_{lh}$

Third band, the spin-orbit or split-off VB separated by an energy $\Delta$ at the $\Gamma$-point from the HH and LH bands

- **Lower level state in the CB**

$\Gamma \Rightarrow$ direct

$\mathbf{k} \neq \mathbf{0} \Rightarrow$ indirect, X-point (AlAs) or near X-point (Si) or L-point (Ge)

- **Effective mass given by the dispersion energy curvature**
  - Isotropic for the CB and the VB in $\Gamma$
  - Anisotropic for the CB in X or L

(longitudinal and transverse effective masses)