Lecture 3 – 25/09/2024

Effective mass approximation

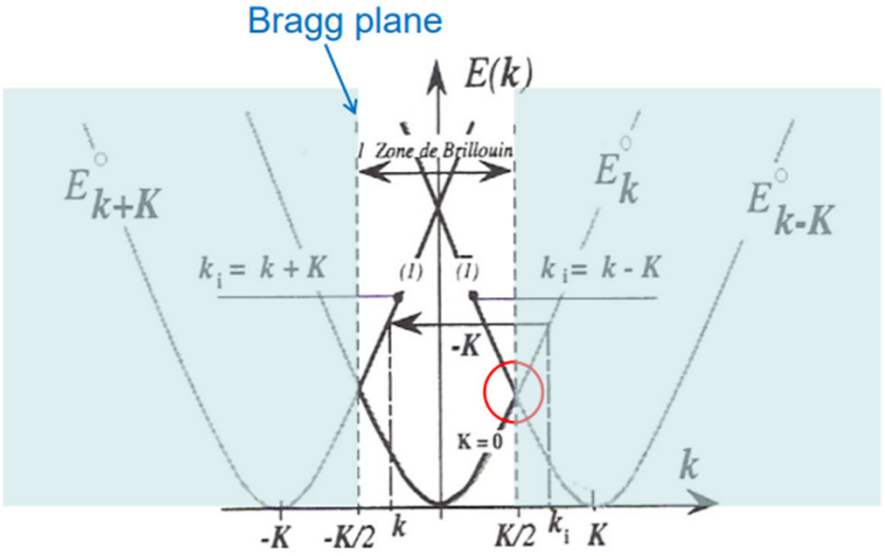
- Electrons
- Holes
- Valence band structure in cubic and hexagonal semiconductors

Summary Lecture 2

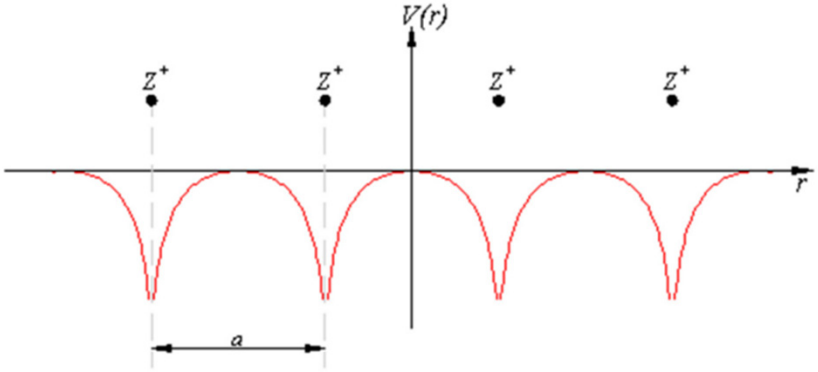
- In a crystal → atoms create a **periodic potential**
- **Kronig-Penney model:** Solving Schrödinger → 2 different solutions for $\psi(r)$ depending on $V(r)$ magnitude
- **Free electrons** **(i.e., $V = 0$)**: Schrödinger solution: $\psi_n(r) = \psi_0 \exp(ikr)$

Energy: $E = \frac{p^2}{2m_0} \rightarrow E_n(k) \equiv$ dispersion curve → gives **electronic band structure**

→ exhibits **symmetry of reciprocal space**



→ reduced zone scheme (≡folding in 1st BZ)
→ description of crystal properties as a whole



Summary Lecture 2

- **Nearly free electron:** electron in crystal with small periodic potential V

→ weak perturbation of free electron energy

Bloch-Floquet theorem: $\psi_k(x) = \sum_G C(k-G)e^{-i(k-G)x}$

→ **Secular equation:** $\left(\frac{\hbar^2 k^2}{2m_0} - E_k\right) C(k) \sum_G V_g C(k-G) = 0$ solutions if det. = 0

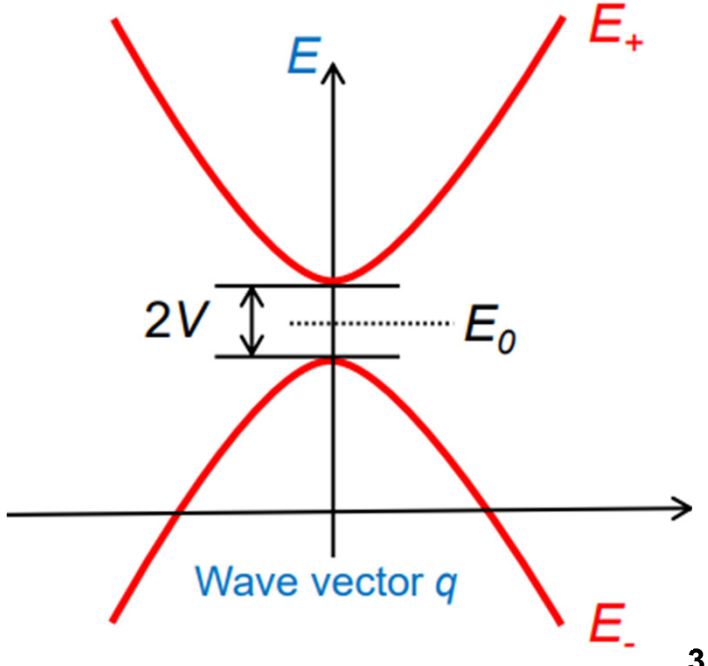
Particular case: k nearby 1st BZ edge (i.e., $k \approx G/2$)

→ $E_\pm = E_0 \pm V + \frac{\hbar^2 q^2}{2m_0}(1 \pm \frac{2E_0}{V})$

→ **Bandgap:** $E_g = 2V(q=0)$

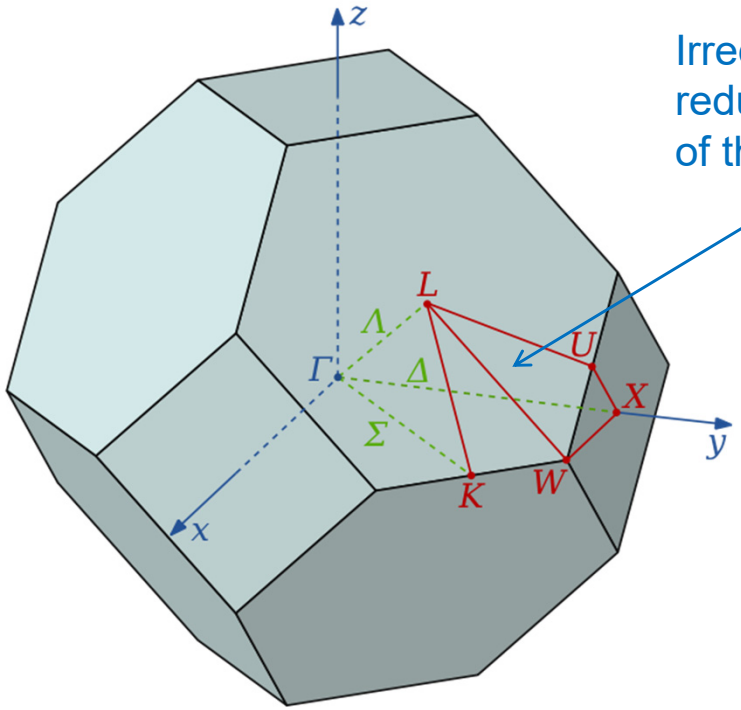
Effective mass: $m_\pm^* = \hbar^2 (\frac{d^2E}{dq^2})^{-1} = m_0 \frac{1}{1 \pm \frac{2E_0}{V}} \approx \pm m_0 \frac{V}{2E_0}$

Smaller E_g → lighter m^*



Brillouin zone (3D case)

High symmetry points: Γ, L, X, and K are within the 1st Brillouin zone (joined by high-symmetry lines)



1st Brillouin zone of the fcc lattice

Irreducible Brillouin zone ≡ first Brillouin zone reduced by all of the symmetries in the point group of the lattice

⇒ Any point of the first Brillouin zone can be accessed from this irreducible representation via a symmetry operation. Hence, knowing the dispersion of electrons along high-symmetry lines will provide you with a complete description of the energy levels accessible to electrons in a crystal (full mapping of electronic band structure)!

$\langle 100 \rangle$ direction: $\dot{\Gamma}\ \overline{\Delta}\ \dot{X}$

$\langle 111 \rangle$ direction: $\dot{\Gamma}\ \overline{\Lambda}\ \dot{L}$

$\langle 110 \rangle$ direction: $\dot{\Gamma}\ \overline{\Sigma}\ \dot{K}$

k.p method

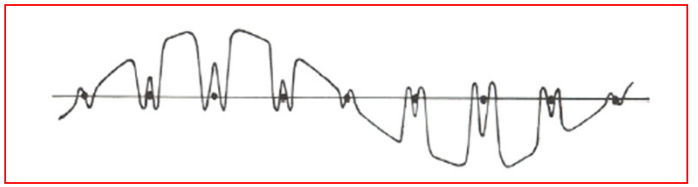
Previous approach (nearly-free electron model) $\Rightarrow$ leads to the formation of forbidden energy band(s) but it remains difficult to predict the exact value of the bandgap or that of the effective masses

***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 $\mathbf{p}^2$ behave as follows:

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

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

One can thus rewrite Schrödinger's equation such that:

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

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

k.p method

Overview

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

$\Rightarrow$ The eigenenergies are then given by:

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

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:

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

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

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

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

Kane matrix element

$\Rightarrow$ describes coupling between electronic states in $\neq$ bands

k.p method

Overview

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

with $$m^* = m_0\left(1 + \frac{P^2}{E_g}\right)^{-1}$$

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**

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

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:

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

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:

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

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:

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

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 Γ point)
- "Hole" in the VB $\Rightarrow$ 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)

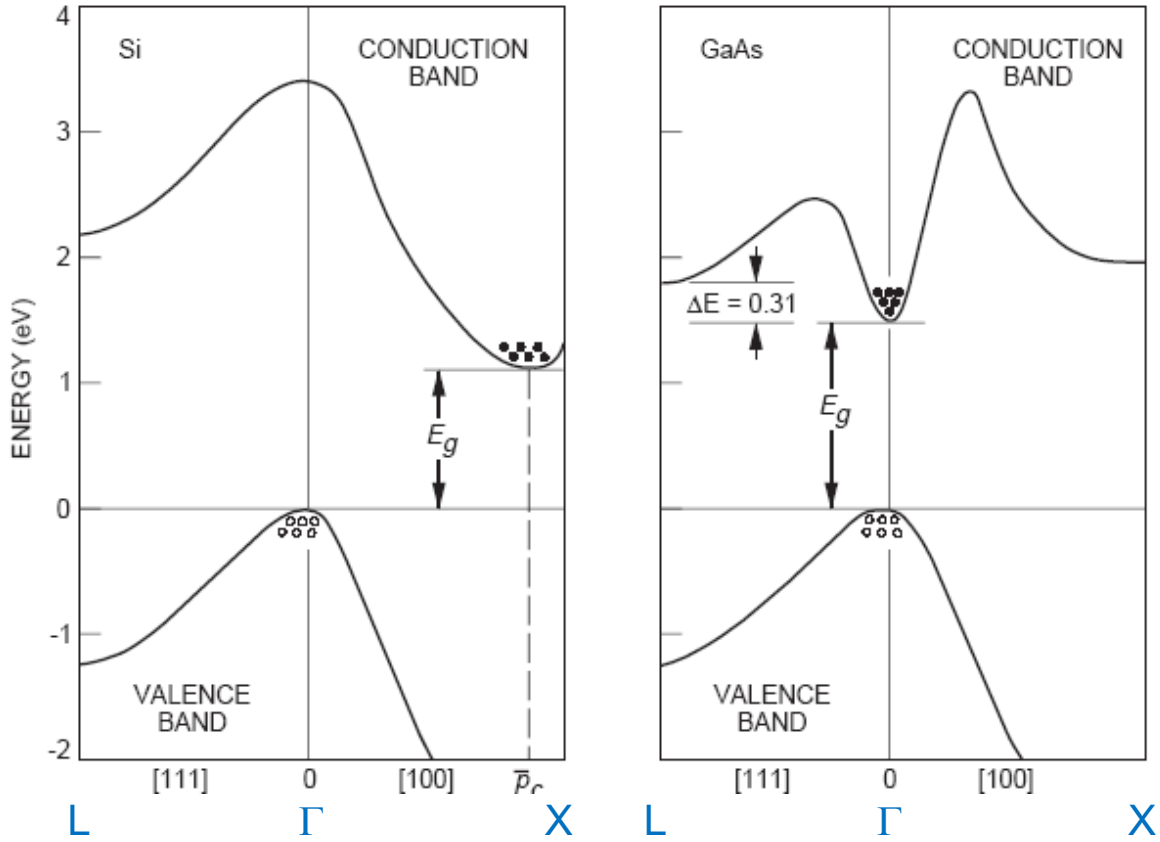
$\Rightarrow$ Isotropic effective mass: the mobility does not depend on the electron motion direction in the crystal

- **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

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

Effective mass



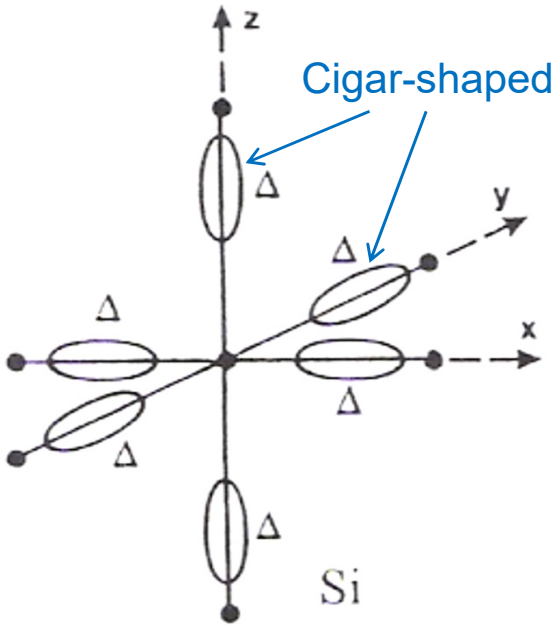
2-band approximation

Effective mass

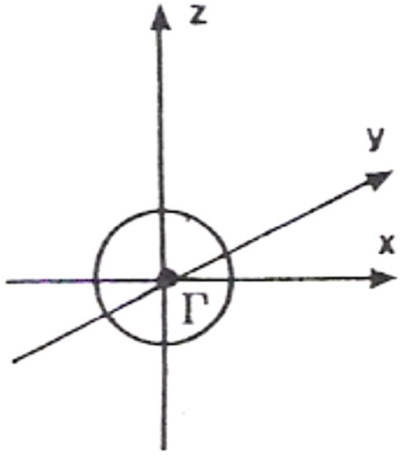
Representation of the constant energy surfaces about the extrema reflecting the effective mass distribution in ***k*-space**

isosurfaces

Cigar-shaped ellipsoids



Anisotropic case

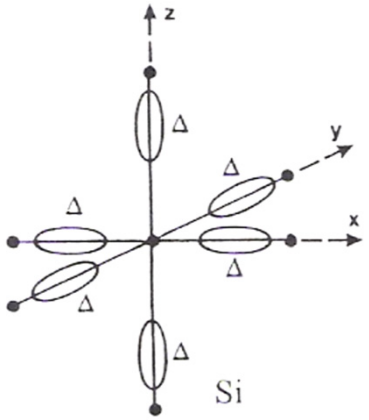


Isotropic case

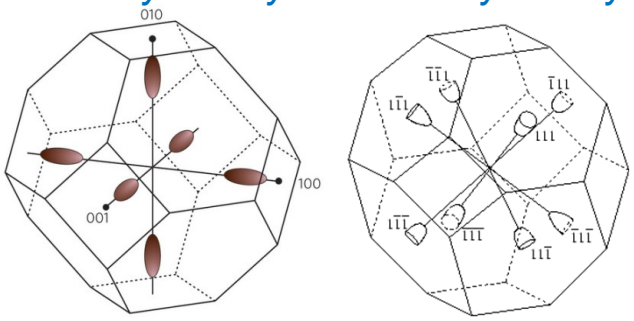
Reciprocal space representation of isosurfaces

Effective mass

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



3-fold symmetry *4-fold symmetry*



X valleys of Si **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 Γ-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 $(6/4m_l^{1/2} m_t)^{2/3}$

Effective mass

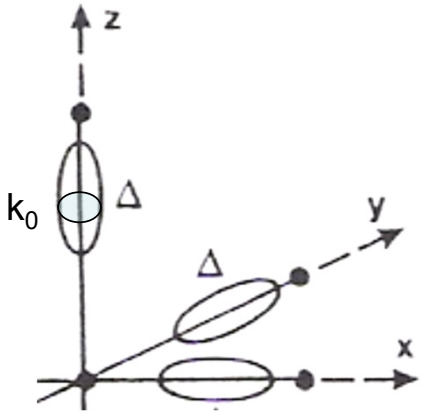
Longitudinal and transverse masses

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

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



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

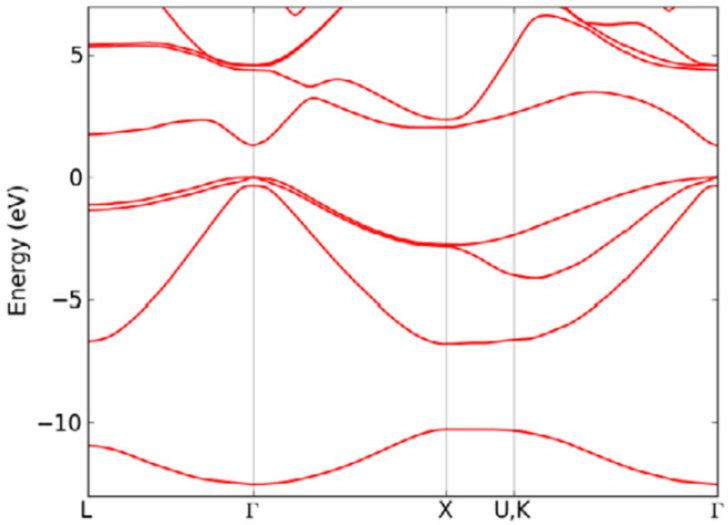
$$E_c(\mathbf{k}) = E_c + \frac{1}{2}\frac{d^2E}{dk_{\parallel}^2}(k_{\parallel} - k_0)^2 + \frac{1}{2}\frac{d^2E}{dk_{\perp}^2}k_{\perp}^2 = E_c + \boxed{\frac{\hbar^2}{2m_l^*}(k_{\parallel} - k_0)^2} + \boxed{\frac{\hbar^2}{2m_t^*}k_{\perp}^2}$$

m_l and m_t are the longitudinal and transverse effective masses, respectively

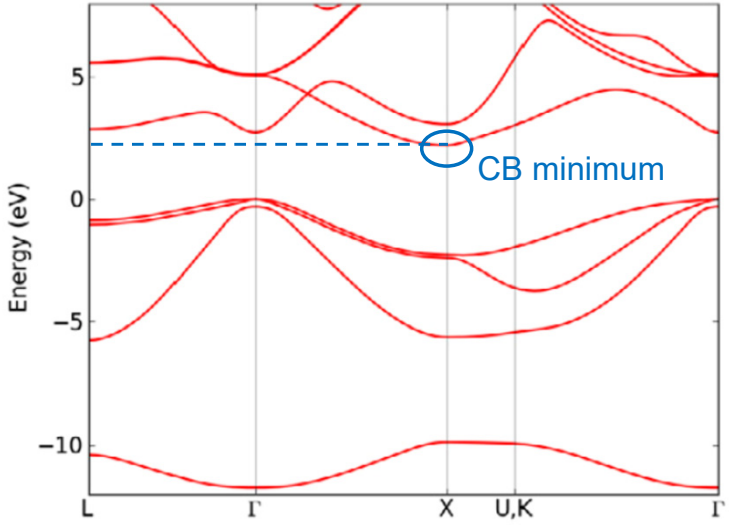
How can you visualize those two masses on the sketch?

Effective mass

Band structure of GaAs



Band structure of AlAs

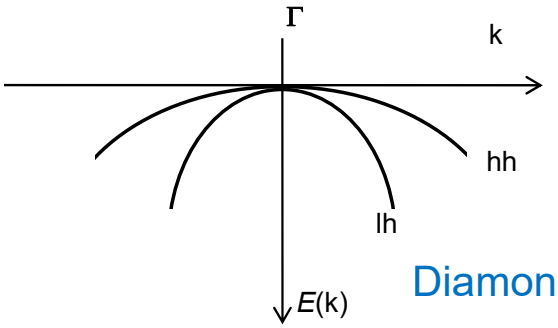


1st principles calculations of quasiparticle band structure

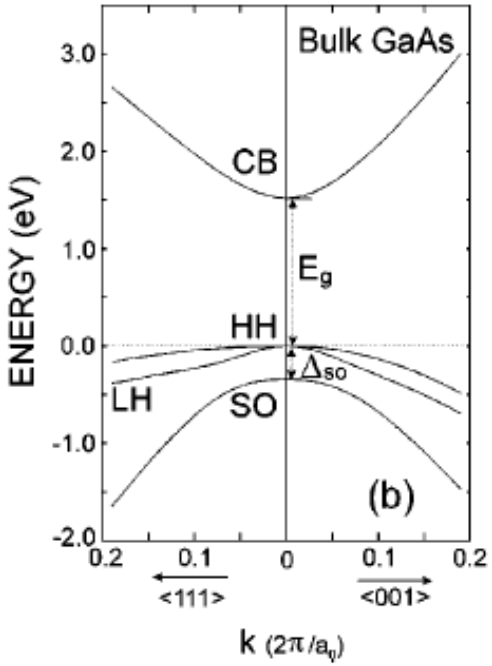
What will be the effective mass of an electron in the AlGaAs alloy?

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
Δ_{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)

> 3100 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:

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

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:

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

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

Two effective masses can be introduced that follow the relations:

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

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 #18 for the trend regarding the magnitude of Δ)

Effects of spin-orbit interaction on the VB

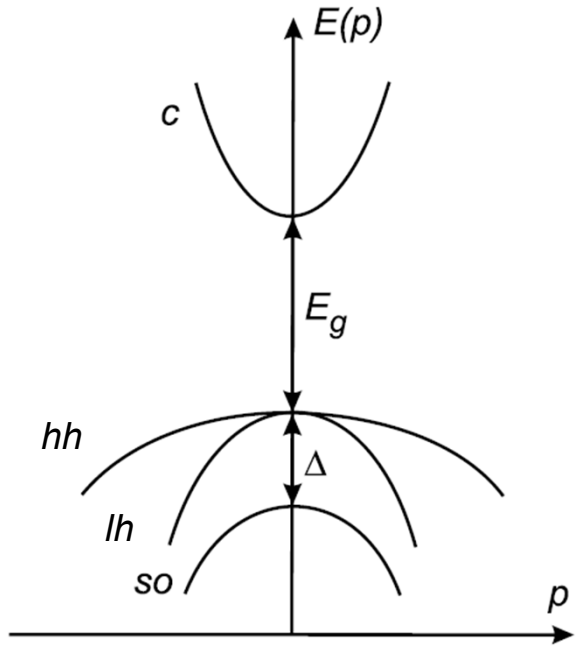
Regarding the $j = 3/2$ state for $\mathbf{p} \neq \mathbf{0}$ for energies $E(p) << \Delta$, a Luttinger Hamiltonian is constructed in a way similar to the case where SO interaction was neglected. The main difference is that 3×3 $L_{x,y,z}$ matrices are now replaced by 4×4 $J_{x,y,z}$ matrices corresponding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

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

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

$$E_{hh}(p) = \left(A + \frac{9B}{4}\right)p^2 = \frac{p^2}{2m_{hh}} \quad \left(J_z = \pm 3/2\right)$$

$$E_{lh}(p) = \left(A + \frac{B}{4}\right)p^2 = \frac{p^2}{2m_{lh}} \quad \left(J_z = \pm 1/2\right)$$

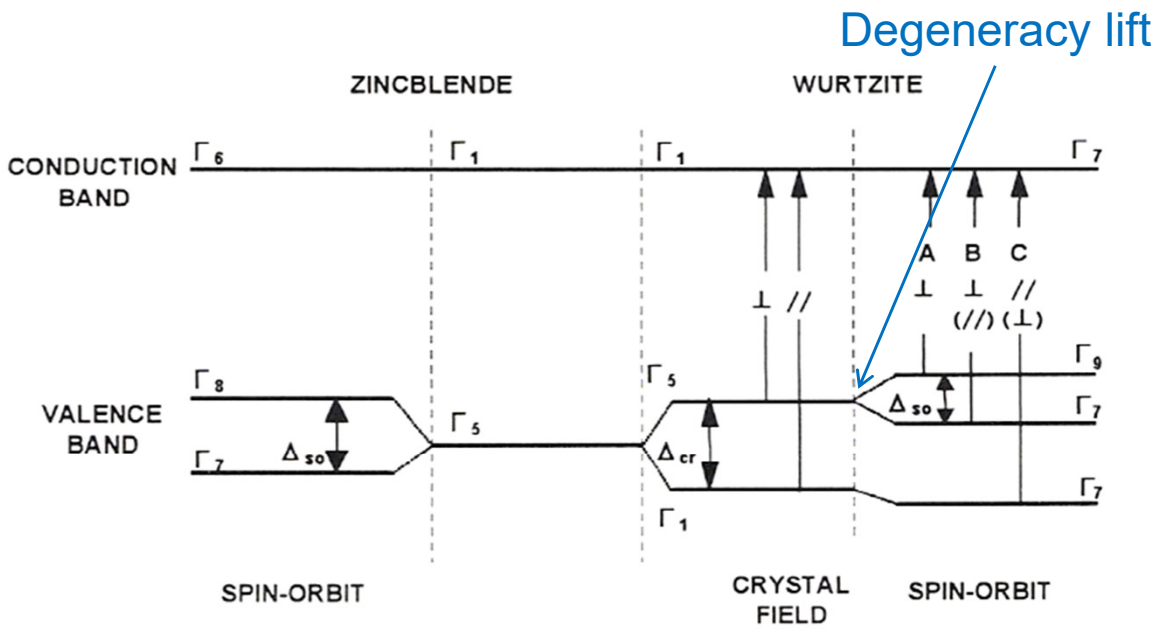


Band structure of a zinc-blende SC near the Γ-point

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)



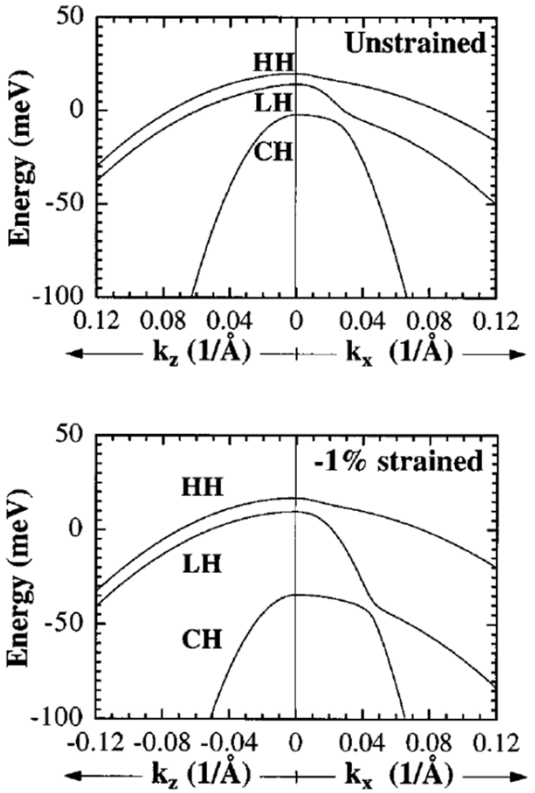


Figure 5.1 Band structures and labeling of respective transition in zincblende and wurtzite GaN. The indications ⊥ and // show that the transition is allowed for the light polarization E perpendicular and parallel to the optic (c) axis, respectively. Parentheses means that the transition is partially allowed. The value Δ_{so} and Δ_{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 Γ (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 Δ at the Γ-point from the HH and LH bands

- **Lower level state in the CB**

  Γ ⇒ direct

  k ≠ **0** ⇒ 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 Γ
  - Anisotropic for the CB in X or L

    (longitudinal and transverse effective masses)