Lecture contents

- Bloch theorem
- k-vector
- Brillouin zone
- Almost free-electron model
- Bands
- Effective mass
- Holes

Translational symmetry: Bloch theorem

One-electron Schrödinger equation (each state can accommodate up to 2 electrons):

$$\left[\frac{p^2}{2m} + V(r) \right] \psi(r) = E \psi(r)$$

If $V(r)$ is a periodic function:

$$V(r) = V(r + R) \qquad R = m_1 a_1 + m_2 a_2 + m_3 a_3$$

The solution is :

$$\psi_k(r) = e^{ikr} u_k(r)$$

where $u_k(r)$ is a periodic function:

$$u_k(r) = u_k(r + R)$$

From:

- Linearity of the Schrödinger equation
- Fourier theorem

Important :

u_k might be not a single valence electron function but is close to linear combination of valence electron wavefunctions

Quasi-wavevector k is analogous to a wavevector for free electrons (V=const)

$$\left| \psi_k(r) \right|^2 = \left| \psi_k(r + R) \right|^2$$

Bloch theorem: consequences

- Introduced *k*-vector quantum number for periodic potential (to enumerate states)

- Momentum is not conserved (not a quantum number), however quasi-momentum is conserved

- *k*-vector can be considered to lie in the first Brillouin zone

- Solution with periodic boundary conditions gives eigen-functions $u_{n,k}$ for a given *k* which forms orthogonal basis (compare with Fourier expansion)

- n –values enumerate bands

- Electron occupying level with wavevector k in the band n has velocity (compare to group velocity)

$$\left[\frac{p^2}{2m} + V(r) \right] \psi(r) = E\psi(r)$$

$$\psi_k(r) = e^{ikr} u_k(r)$$

$$E = \frac{\hbar^2}{2m} \left(k + n\frac{2\pi}{a} \right)^2$$

$$\left[\frac{\hbar^2}{2m} \left(\frac{1}{i}\nabla + k \right)^2 + V(r) \right] u_k(r) = E_k u_k(r)$$

$$u_k(r) = u_k(r + R)$$

$$\Longrightarrow u_{n,k}(r), E_{n,k}$$

$$\Longrightarrow v_n(k) = \frac{1}{\hbar} \nabla_k E_n(k)$$
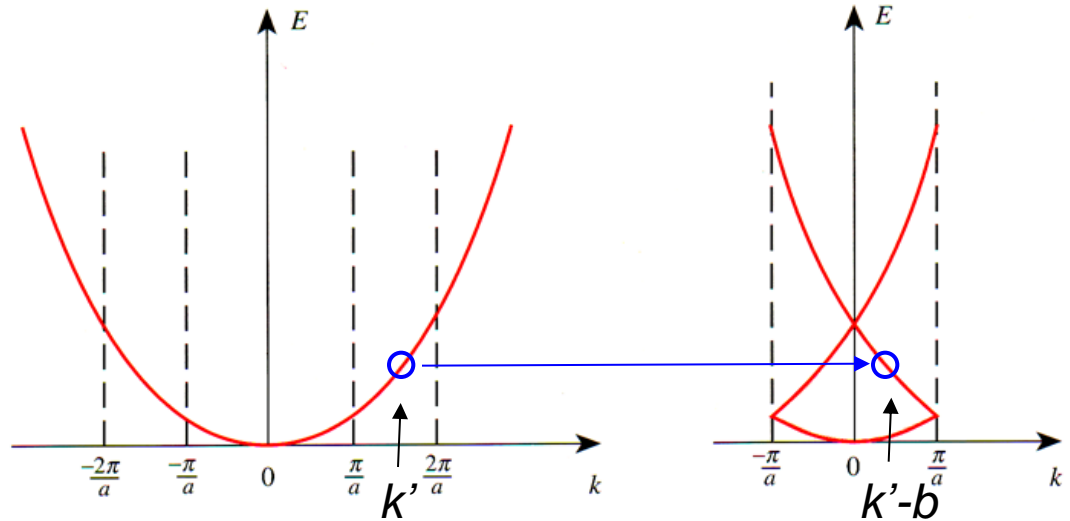
Reciprocal space (1D)

Wavefunction of an electron in crystal :
$$\psi_k(r) = e^{ikr} u_k(r)$$

1D free electrons "band structure" is:

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

$$\psi_{k'}(r) = e^{ik'r} u_{k'}(r) = e^{ikr}\left(e^{ibr} u_{k'}(r) \right) \equiv e^{ikr} u_{2,k}(r)$$
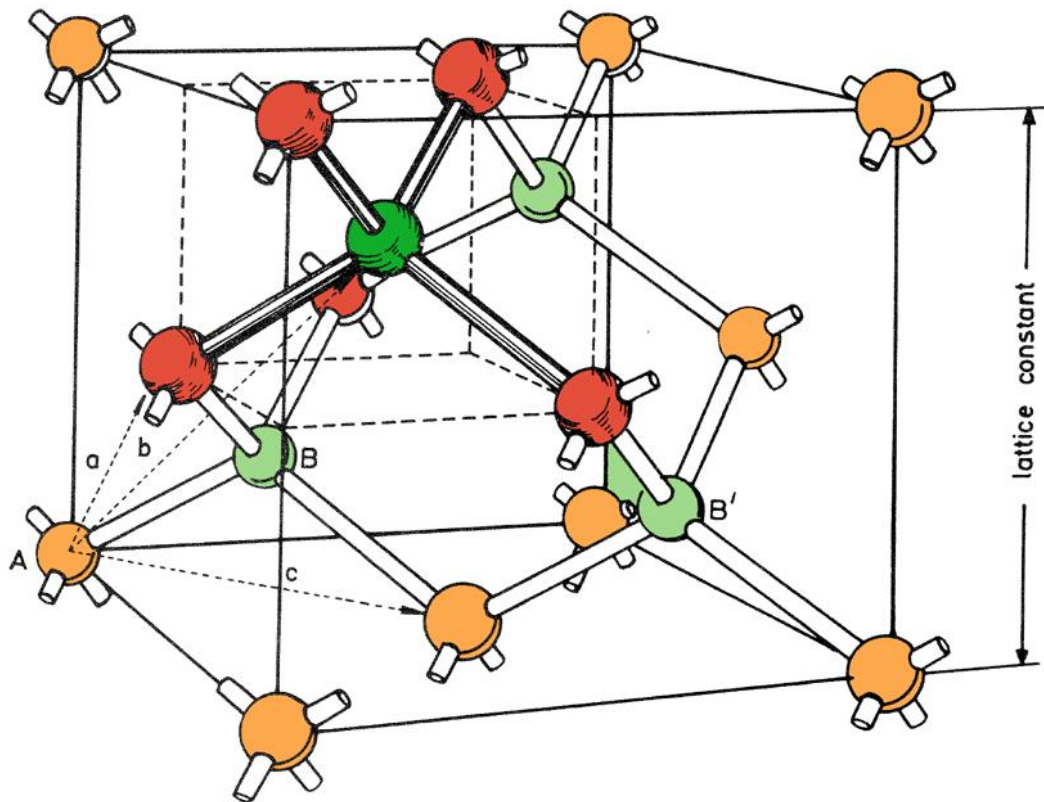
2nd band

periodic function

1D reciprocal lattice vector : $b = \dfrac{2\pi}{a_0} m$

First Brillouin zone: $-\dfrac{\pi}{a_0} < k \leq \dfrac{\pi}{a_0}$
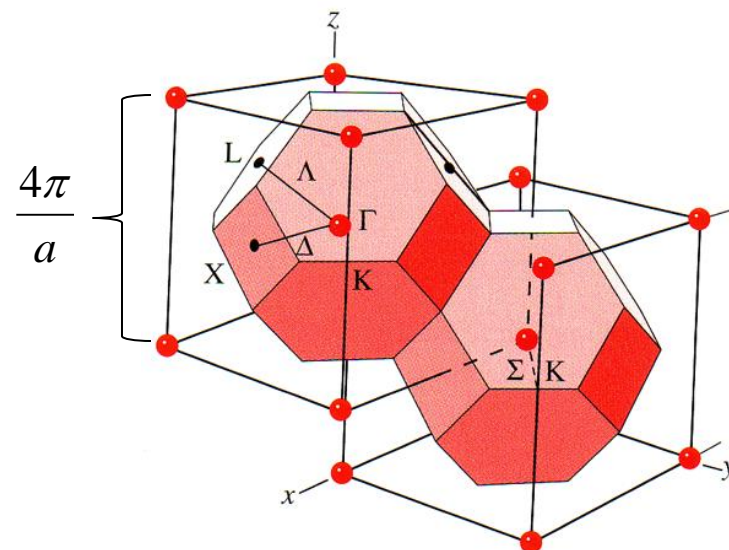
Diamond or zinc-blende structures

- 4(Ga) + 4(As)=8 atoms in a cubic unit cell
- 1+1 =2 atoms in a primitive unit cell

Primitive unit cell in a reciprical space (1st Brillouin zone)

$$b = m_1 b_1 + m_2 b_2 + m_3 b_3$$

$$b_1 = 2\pi \frac{(a_2 \times a_3)}{(a_1 \times a_2) \bullet a_3}, b_2, b_3 = ...$$
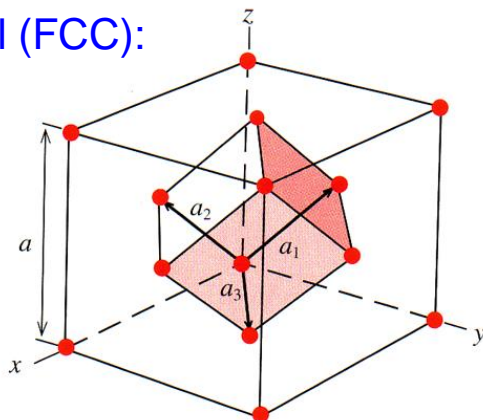
Brillouin zone (FCC):

$\frac{4\pi}{a}$

Primitive unit cell (FCC):

$$a_1 = \frac{a_0}{2}(0,1,1)$$

$$a_2 = \frac{a_0}{2}(1,0,1)$$

$$a_3 = \frac{a_0}{2}(1,1,0)$$

Two wells: Illustration of Bloch Theorem
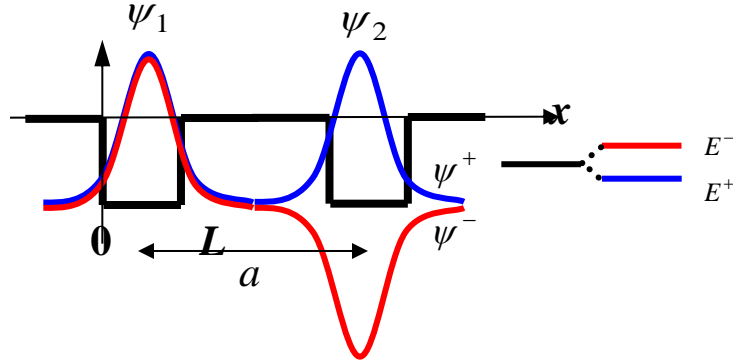
$$\Delta E^{\pm} \approx \langle \psi_1 | V_2 | \psi_1 \rangle \pm \langle \psi_1 | V_1 | \psi_2 \rangle$$

$$\psi^{\pm} \approx \frac{1}{\sqrt{2}} (\psi_1 \pm \psi_2)$$

$$\psi^+ = \frac{1}{\sqrt{2}} [\psi_0(x) + \psi_0(x-a)]$$

$$\boxed{\text{How?}} \Rightarrow \quad \psi_k(r) = e^{ikr} u_k(r)$$

$$\psi^- = \frac{1}{\sqrt{2}} [\psi_0(x) - \psi_0(x-a)]$$

$$\boxed{k = 0, \frac{\pi}{a}}$$

$$\psi_k = \frac{1}{\sqrt{2}} \sum_{m=0}^{1} e^{ikma} \psi_0(x-ma) =$$

$$= \frac{1}{\sqrt{2}} \sum_{m=0}^{1} e^{ik(ma+x-x)} \psi_0(x-ma) = \frac{1}{\sqrt{2}} e^{ikx} \sum_{m=0}^{1} e^{-ik(x-ma)} \psi_0(x-ma) = \begin{cases} \frac{1}{\sqrt{2}} [\psi_0(x) + \psi_0(x-a)], \ \text{k=0} \\ \frac{1}{\sqrt{2}} [\psi_0(x) - \psi_0(x-a)], \ \text{k=}\frac{\pi}{2} \end{cases}$$

$$u_k(x) - periodic!$$

$$k \quad and \quad k + \frac{2\pi}{a} \quad are \quad equivalent$$

Free electrons

- Time-independent Schrödinger equation: $\hat{H}\psi(r) \equiv \left[-\dfrac{\hbar^2}{2m}\Delta + V(r) \right]\psi(r) = E\psi(r)$ $V(r) = V_0 = const$

- Solution - plane wave $\psi(r) = e^{ik'r}$ with energy $E = V_0 + \dfrac{\hbar^2 k'^2}{2m}$

- Though free electron wave functions do not depend on the structure of solid, they can be written in the form of Bloch functions
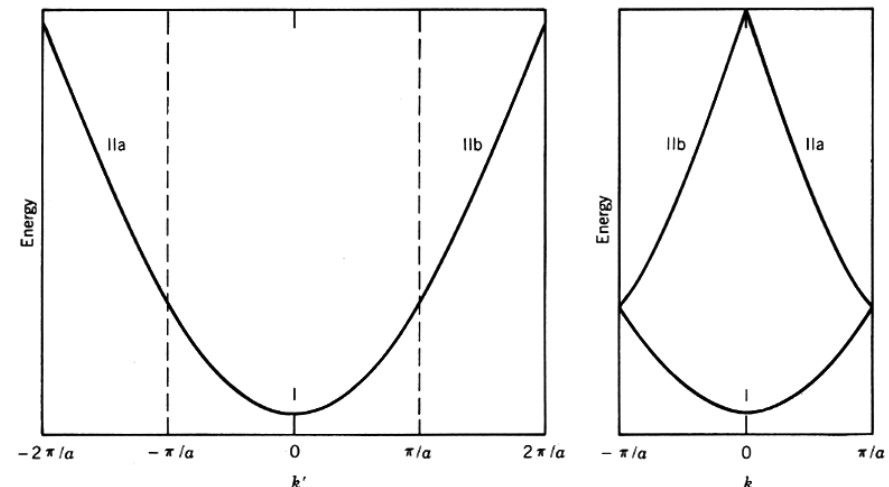 - For any propagation vector k' we can find
    $k' = k + G$ in the first Brillouin zone

Reciprocal lattice point nearest **k'**
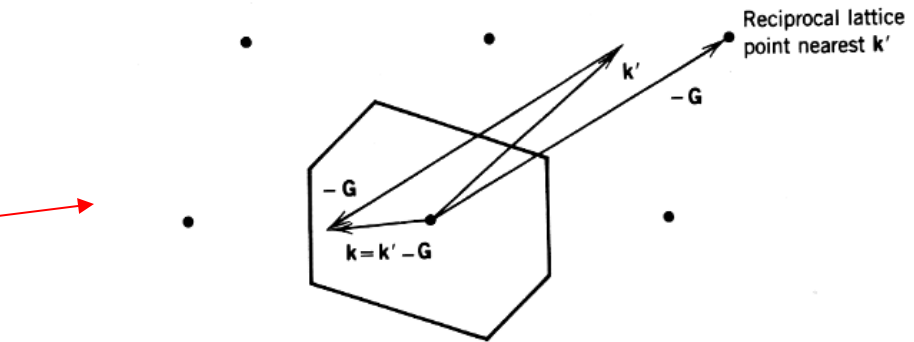
- Then wave function (Bloch function) and energy:

  periodic function

  $$\psi_k(r) = e^{ikr}e^{iGr}$$

  $$E = V_0 + \frac{\hbar^2}{2m}\left| k + G \right|^2$$

- For these wave functions we can plot the band diagram, which become periodic with $2\pi/a$

Nearly free electrons: bandgap

- Introduce weak periodic potential

$$\left[-\frac{\hbar^2}{2m}\Delta + V(r)\right]\psi(r) = E\psi(r) \qquad V(r+g) = V(r)$$

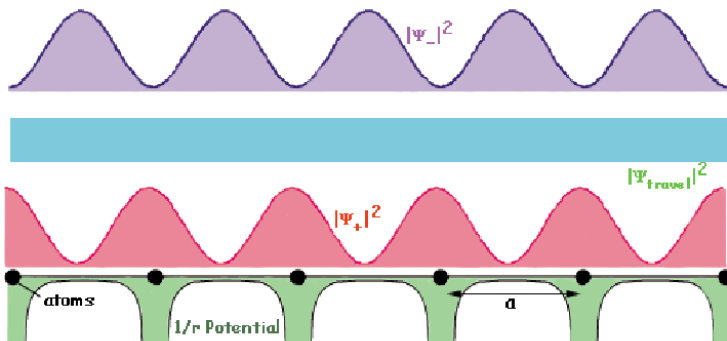or in a Fourier series $\quad V(r) = \sum_G V_G e^{iGr}$

- Let's simplify the problem: 1D potential with just one Fourier component:

$$V(r) = V_1 \cos\frac{2\pi x}{a}$$

- Electrons are waves : Bragg reflection occurs at

$$k = n\frac{\pi}{a}, \quad p = \pm 1, \pm 2...$$

- In quantum mechanics degenerate states $k = \pm\dfrac{\pi}{a}$ can split when perturbation is applied:

- Wave functions corresponding to split states will be linear combinations of $k = \pm\dfrac{\pi}{a}$:

$|\Psi_-|^2$

$|\Psi_{trave}|^2$

$|\Psi_+|^2$

$e^{ikx} - e^{-ikx}$

$\sim \sin(kx)$

$e^{ikx} + e^{-ikx}$

$\sim \cos(kx)$

atoms

1/r Potential

a

$E = \dfrac{\hbar^2}{2m}k^2$

$\mathcal{E}$

Free electron theory

Energy gap

$-3\pi/a \quad -2\pi/a \quad -\pi/a \quad 0 \quad \pi/a \quad 2\pi/a \quad 3\pi/a$ $\quad k$

3rd zone 2nd zone 1st zone 2nd zone 3rd zone
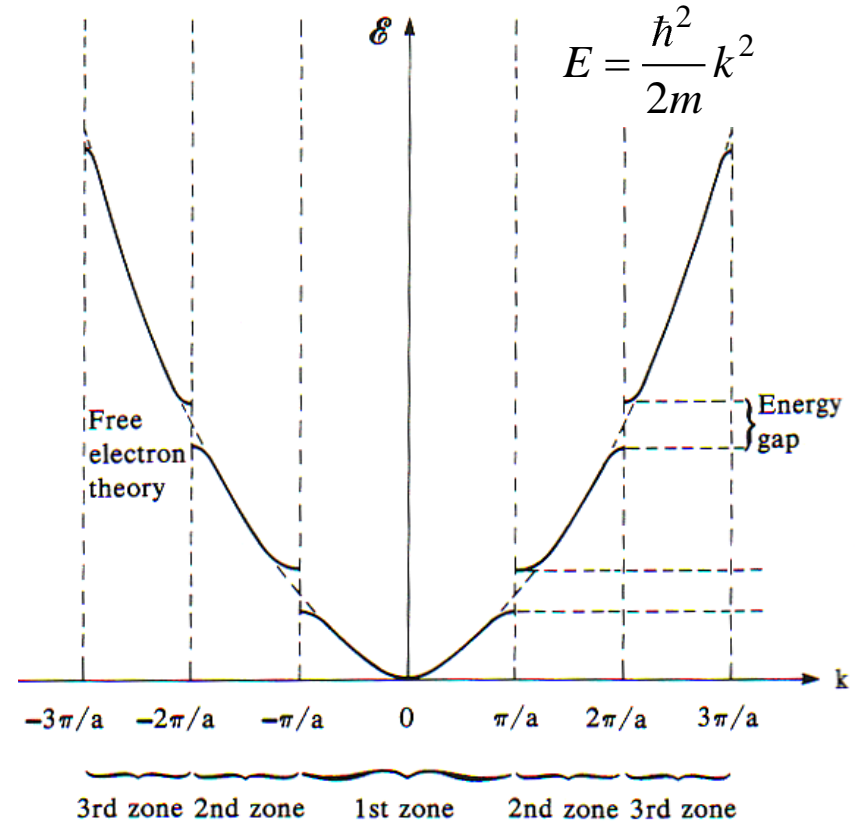
Nearly free electrons: Bandgap

- By first-order perturbation theory:

$$\Delta E^{\pm} \approx \left\langle \psi^{\pm} \,\big|\, V_1 \cos\frac{2\pi x}{a} \,\big|\, \psi^{\pm} \right\rangle$$

- Calculating the integral, find bandgap:

$$E_g = E^- - E^+ = \frac{2V_1}{L}\int_0^L \cos\frac{2\pi x}{a}\left(\cos^2\frac{\pi x}{a} - \sin^2\frac{\pi x}{a}\right)dx = V_1$$

- Free electrons (plane waves) don't interact with the lattice much until wavevector becomes comparable with $1/a$, then they are Bragg reflected and we have interference between a plane wave and its oppositely directed counterpart.

- These superpositions are *standing waves* with the same kinetic energy, but total energy is different
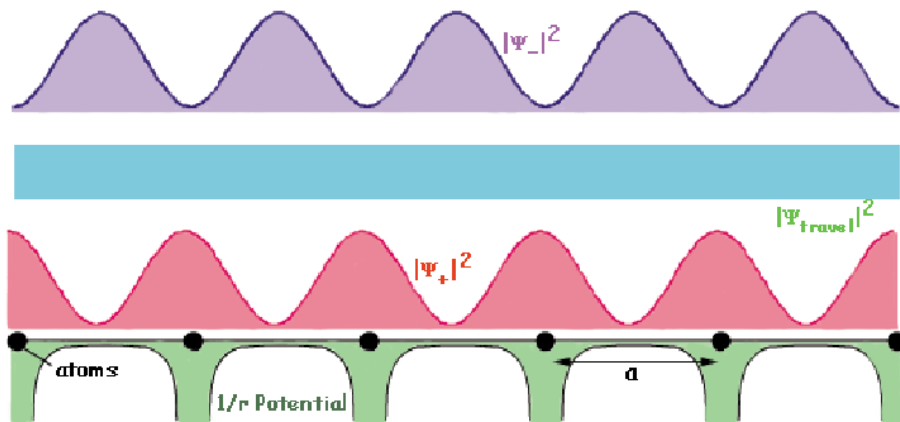
$$e^{ikx} - e^{-ikx}$$

$$\sim \sin(kx)$$

$$e^{ikx} + e^{-ikx}$$

$$\sim \cos(kx)$$
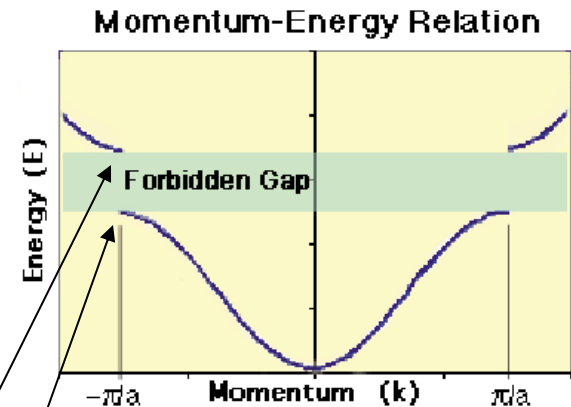
Nearly free electrons: 2D bands

The first three Brillouin zones of a simple square lattice
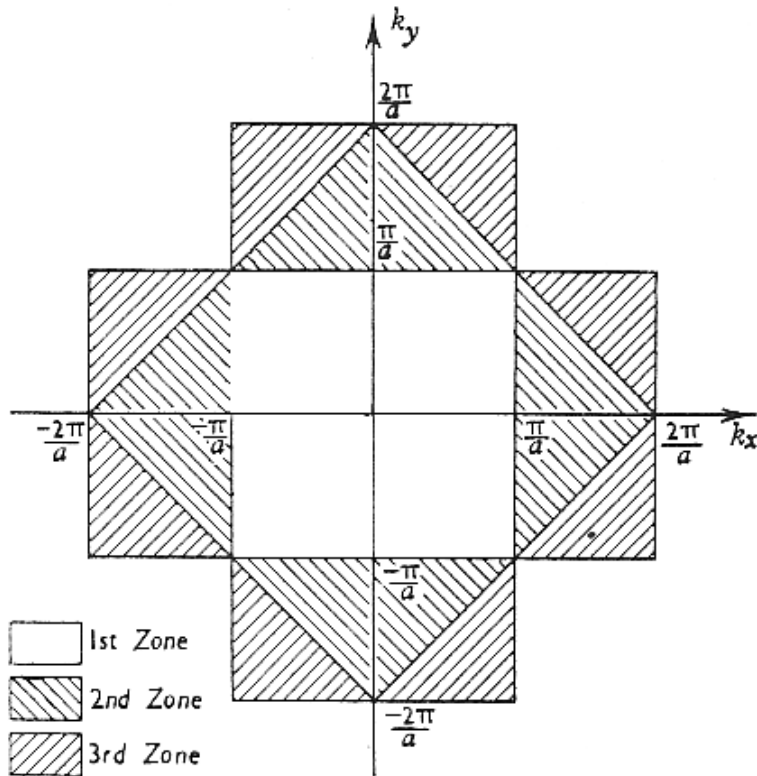
E-k curves for three different directions for parabolic band

Ist Zone
2nd Zone
3rd Zone
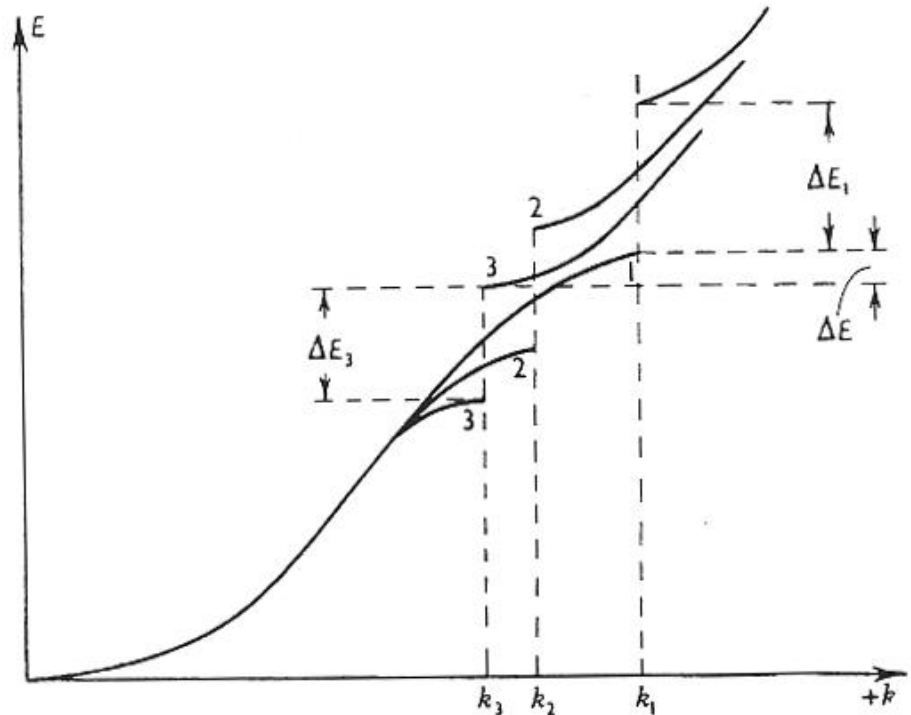
Irrelevant to dimensionality, the following properties are valid:

- Within the first zone lie all points of allowed reduced wave vector
- "One-zone" and "many zone" descriptions are alternatives
- All the zones has the same "volume"
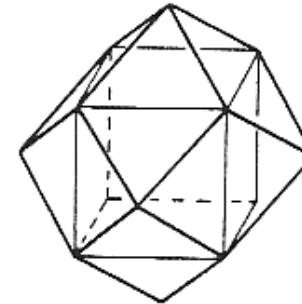- The zone boundaries are the points of energy discontinuity

From Cusack 1963

Nearly free electrons: 3D bands

First Brillouin zones for various 3D structures

Fig. 7.5b. First two zones of a simple cubic lattice.
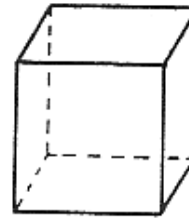
1st

2nd
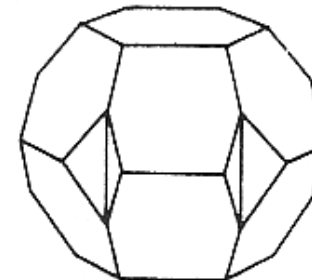
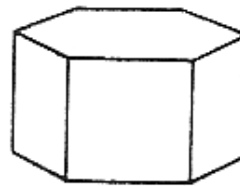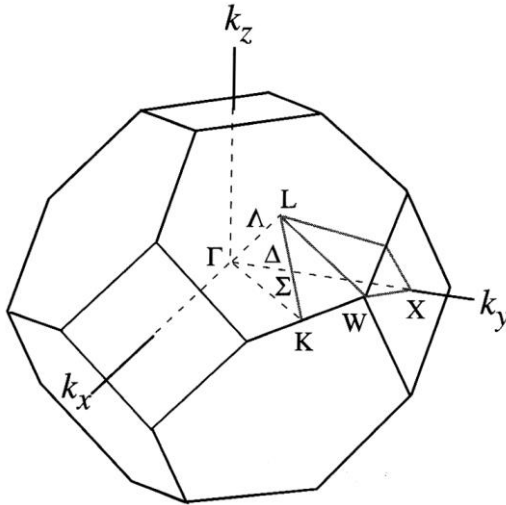Fig. 7.5c. First zones of body- and face-centred cubic lattices.
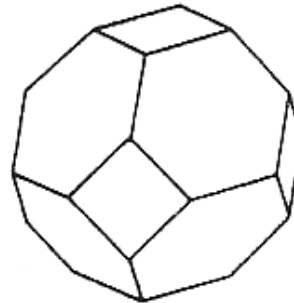
Face centred
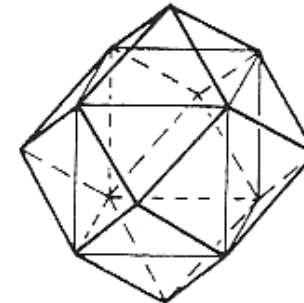
Body centred

Fig. 7.5d. First two zones of a hexagonal lattice.

From Cusack 1963

Nearly free electrons: 3D bands

First Brillouin zone for fcc structure

Free electron bands of fcc structure
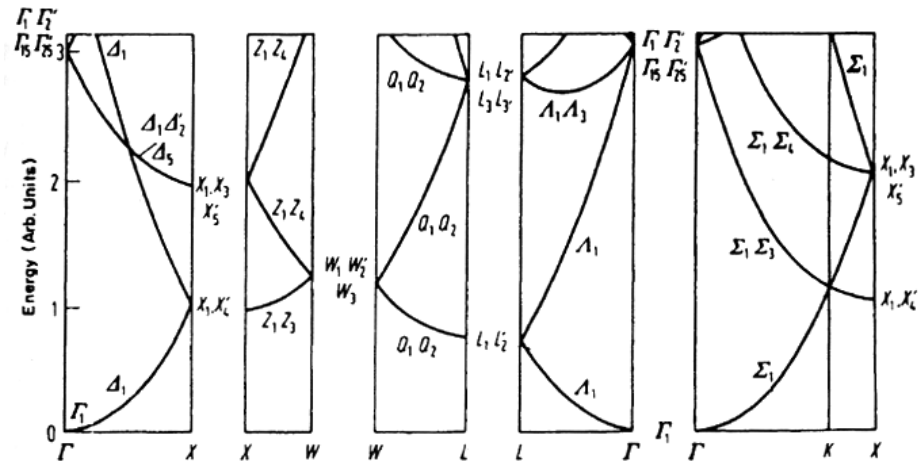
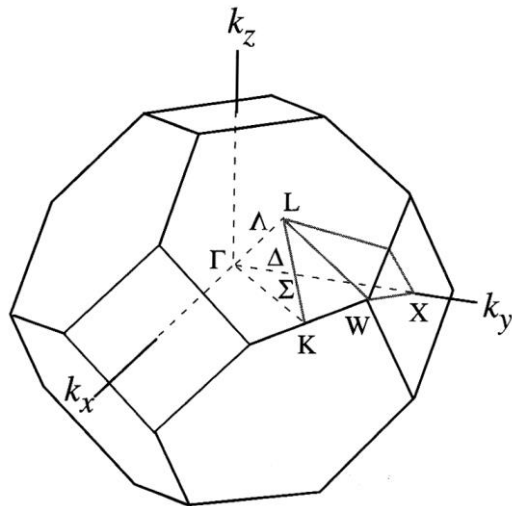Electron bands in fcc Al compared to free electron bands (dashed lines)
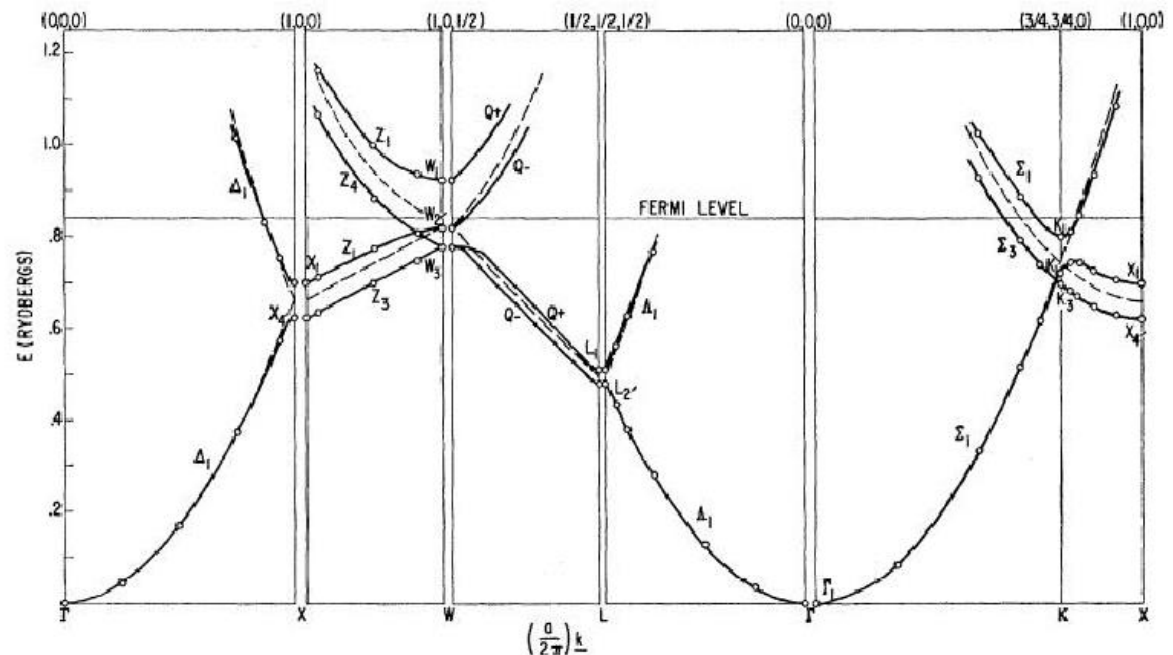
Γ- point: $(0,0,0)$

X- point: $\frac{2\pi}{a}(1,0,0)$

L- point: $\frac{\pi}{a}(1,1,1)$

K- point: $\frac{2\pi}{a}\left(\frac{3}{4},\frac{3}{4},0\right)$

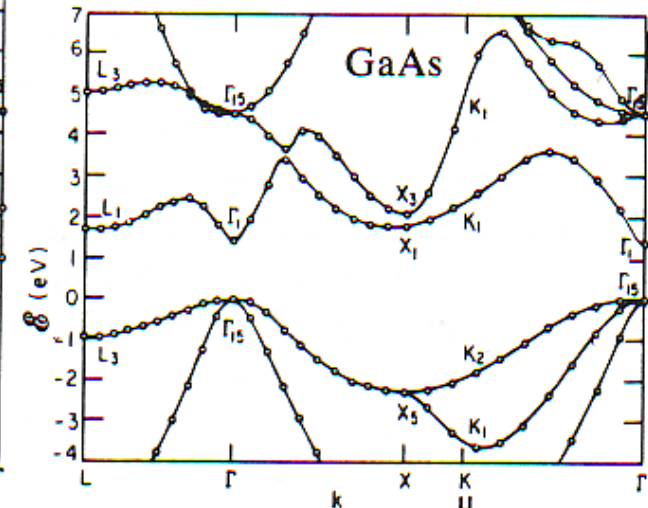W- point: $\frac{2\pi}{a}\left(1,\frac{1}{2},0\right)$

From Hummel, 2000

With diamond structure

With zinc-blende structure

Γ- point: $(0,0,0)$

X- point: $\frac{2\pi}{a}(1,0,0)$

L- point: $\frac{\pi}{a}(1,1,1)$

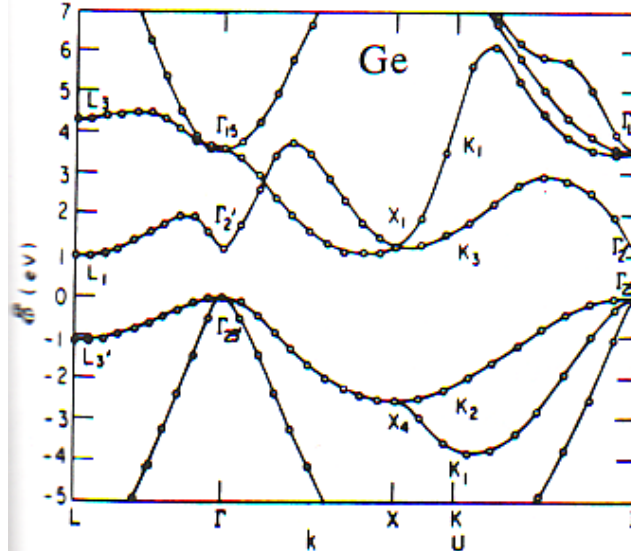K- point: $\frac{2\pi}{a}\left(\frac{3}{4},\frac{3}{4},0\right)$

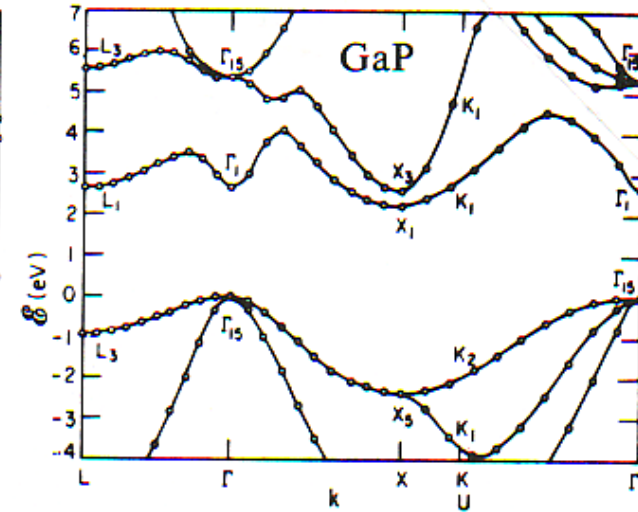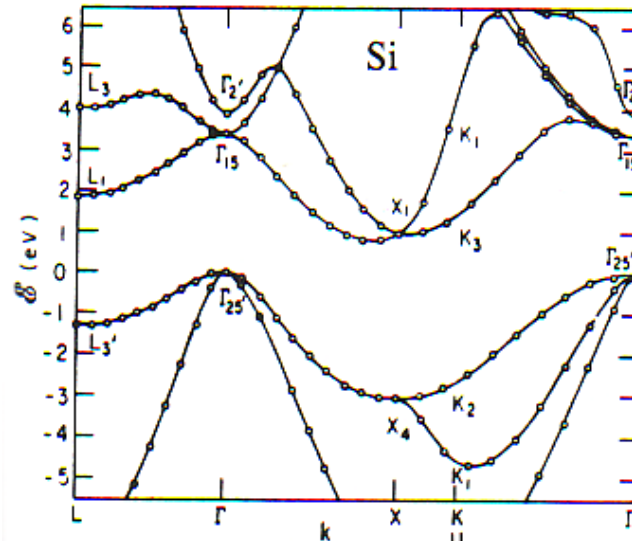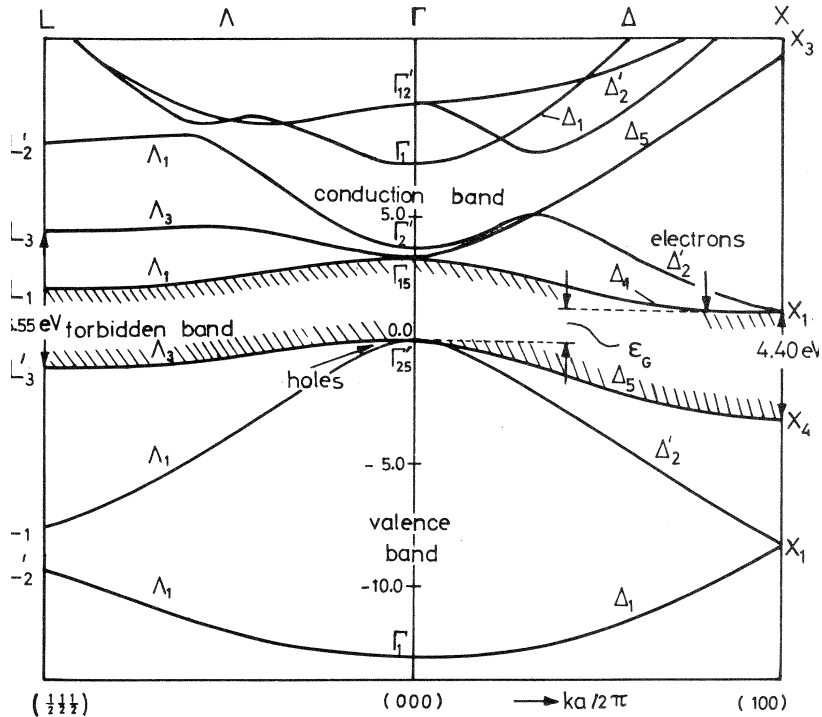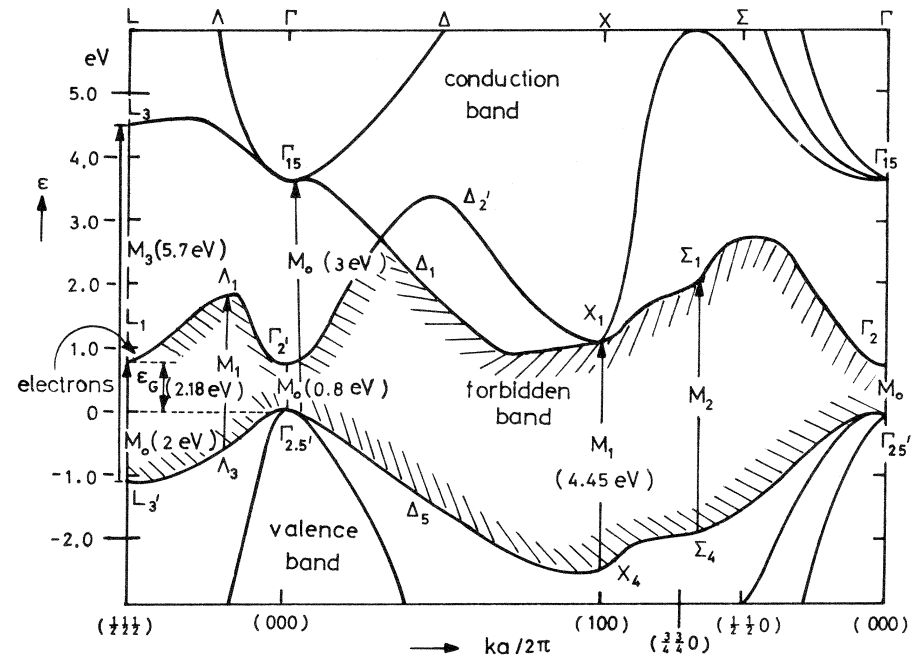W- point: $\frac{2\pi}{a}\left(1,\frac{1}{2},0\right)$
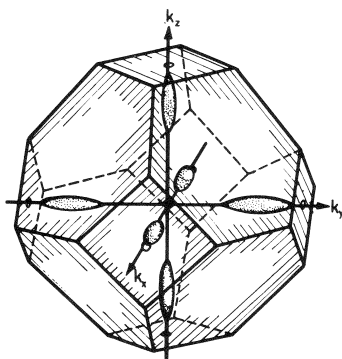
From Burns, 1985

Band-structures of Si and Ge

Energy band structure of silicon

Energy band structure of germanium.

Surfaces of constant energy in $\vec{k}$-space for
the conduction band edge of silicon.
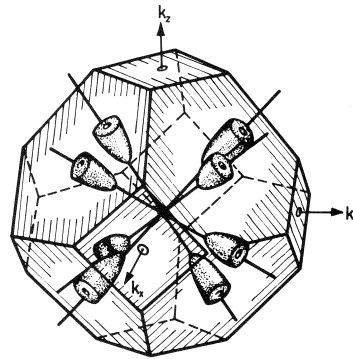
Surfaces of constant energy in $\vec{k}$-space for
the conduction band edge of germanium:
8 half-ellipsoids of revolution centered
at L points on the zone boundary

	m_ℓ^*	m_t^*	$\bar{m}_{\ell h}^*$	$\bar{m}_{hh}^*$
Si	0.92	0.19	0.16	0.52
Ge	1.59	0.082	0.043	0.34

Most essential bands in diamond/ZB semiconductors

GaAs

From www.ioffe.ru
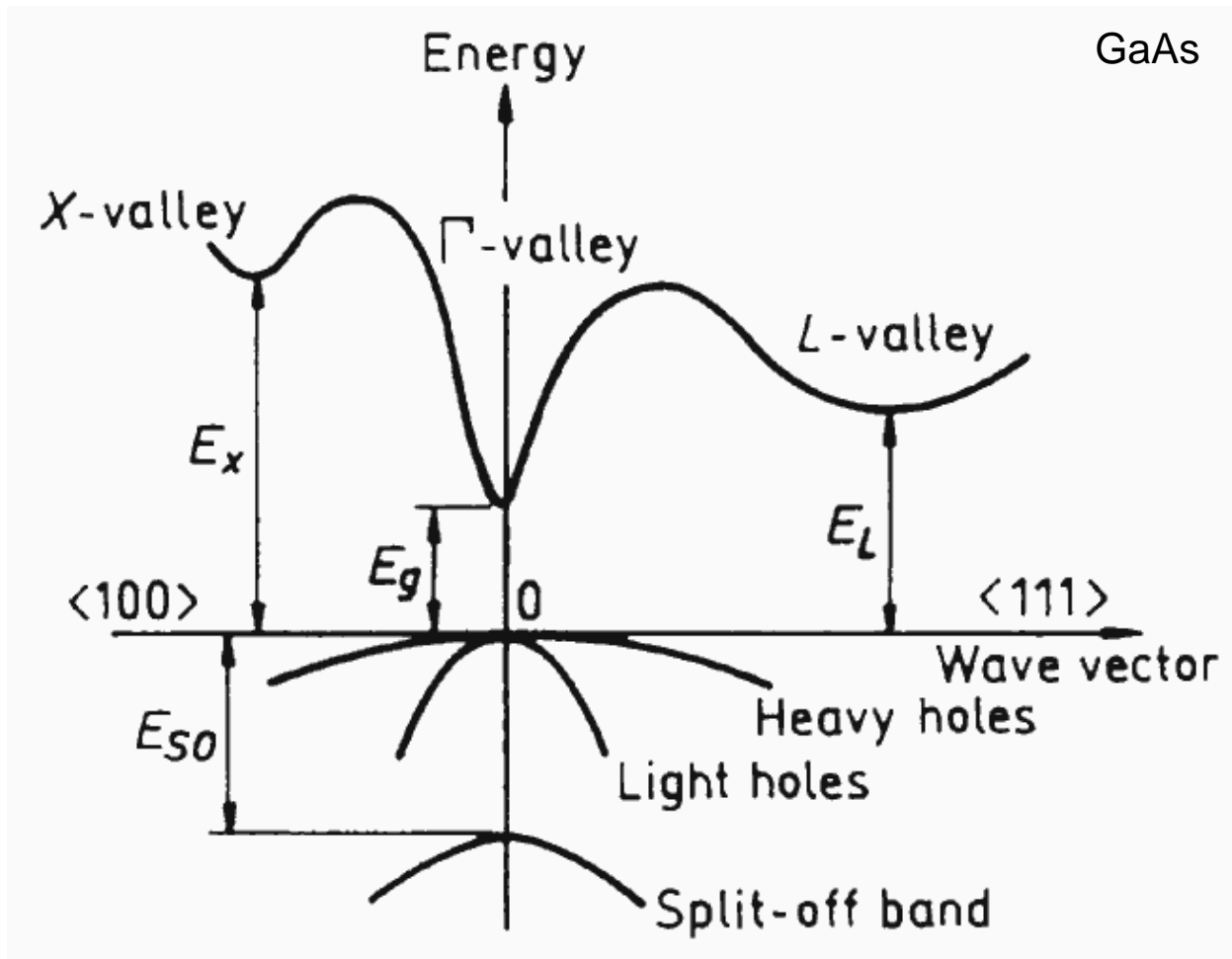
Free electrons and crystal electrons

Free electrons

Wave function: $\psi_k(r) = \dfrac{1}{\sqrt{V}} e^{ikr}$

Kinetic energy: $E = \dfrac{\hbar^2 k^2}{2m}$

Velocity or group velocity:

$$\bar{v} = \int \psi^* \left(-\frac{i\hbar}{m} \nabla \right) \psi \, dr = \frac{\hbar k}{m}$$

Dynamics (F – force):

$$\frac{dv}{dt} = \frac{1}{m} F$$

Force equation:

$$F = \frac{dp}{dt} = \hbar \frac{dk}{dt}$$

Electrons in solid

Wave function: $\psi_k(r) = e^{ikr} u_k(r)$

Dispersion near band extremum (isotropic and parabolic): $E = \dfrac{\hbar^2 (k - k_0)^2}{2m^*}$

Group velocity: $v = \dfrac{1}{\hbar} \nabla_k E(k)$

Velocity at band extremum: $v = \dfrac{\hbar(k - k_0)}{m^*}$

Dynamics in a band:

$$\frac{dv}{dt} = \frac{1}{\hbar} \nabla_k \frac{dE}{dt} = \frac{1}{\hbar} \nabla_k (Fv) = \frac{1}{\hbar^2} (\nabla_k \nabla_k E) F$$

$$\frac{dv}{dt} = \frac{1}{m^*} F; \qquad \frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k^2} \qquad \text{(if m* isotropic and parabolic)}$$

Force equation:

$$\frac{dE(k)}{dt} = \nabla_k E \frac{dk}{dt} = Fv \qquad\qquad F = \hbar \frac{dk}{dt}$$

Holes

- It is convenient to treat top of the uppermost valence band as <u>hole</u> states

- <u>Wavevector of a hole</u> = total wavevector of the valence band (=zero) minus wavevector of removed electron:

$$k_h = 0 - k_e$$

Hole energy:

- <u>Energy of a hole</u>. Energy of the system increases as missing electron wavevector increases:

$$E_h(k_h) = -E_e(k_e)$$

Missing electron energy:

$$E_e(k_e) = E_v + \frac{\hbar^2 k_e^2}{2m_e^*}$$

- <u>Mass of a hole</u>. Positive! (Electron effective mass is negative!)

$$m_h^* = -m_e^* \qquad E_h(k_h) = -E_v + \frac{\hbar^2 k_h^2}{2m_h^*}$$

- <u>Group velocity</u> of a hole is the same as of the missing electron

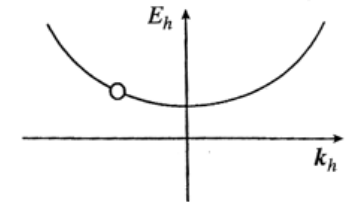$$v_h = \frac{1}{\hbar}\nabla_k E_h(k_h) = \frac{1}{\hbar}\nabla_k \left[-E_e(-k_e)\right] = v_e$$

- <u>Charge of a hole</u>. Positive!
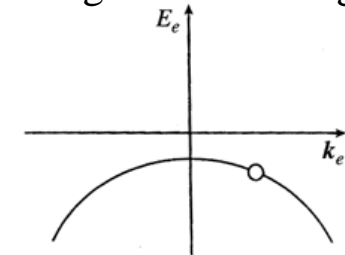
$$\hbar \frac{dk_e}{dt} = -e\mathcal{E}$$

$$e_h = -e_e = +e$$

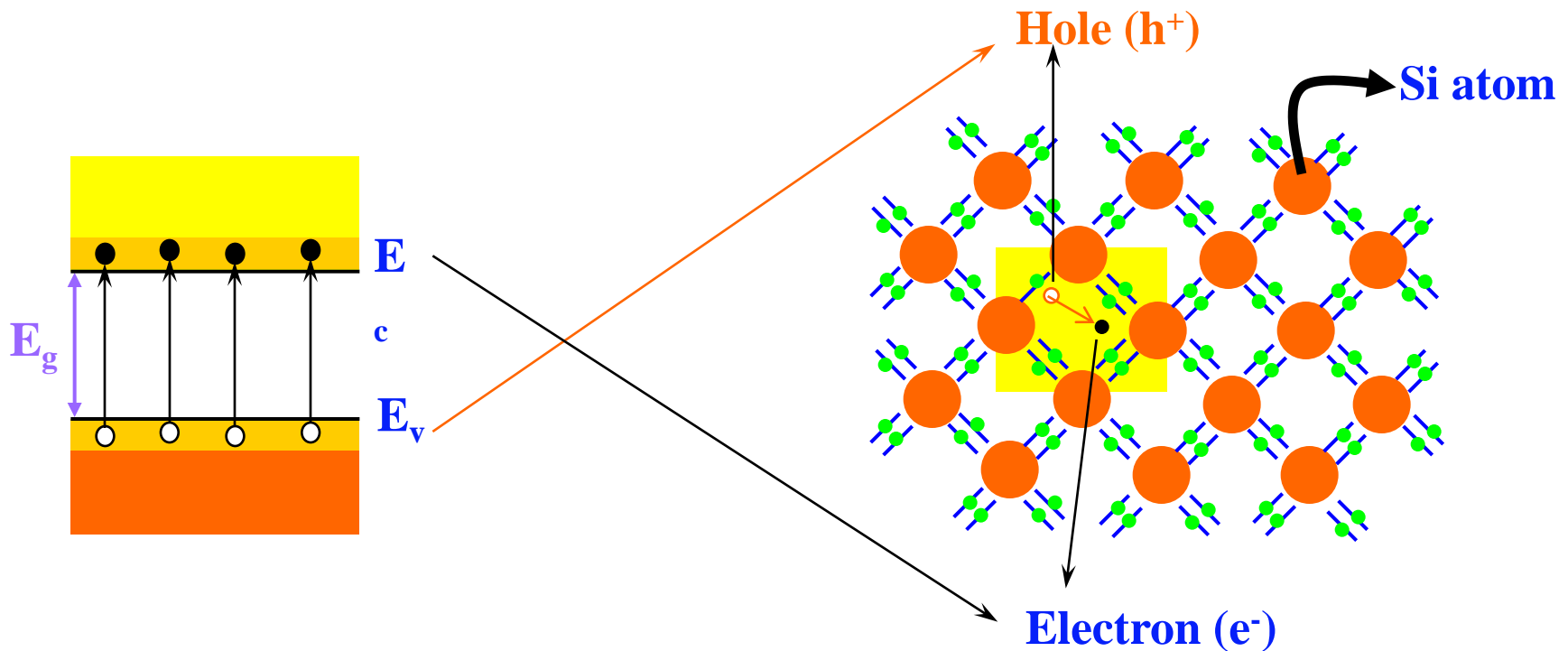$$\hbar \frac{dk_h}{dt} = e_h \mathcal{E}$$

Example: electron-hole pairs in semiconductors

Hole (h$^+$)

Si atom

E_g

E_c

E_v

Electron (e$^-$)

EHP generation : Minimum energy required to break covalent bonding is E_g.

Charge carriers in a crystal

$$F = ma = +qE$$

hole

$$F = ma = -qE$$

electron

Charge carriers in a crystal are not completely free. ➔ Need to use effective mass NOT REST MASS !!!

E

Si atom

V

-   **+**