Optical Properties of Solids: Lecture 7

Stefan Zollner

New Mexico State University, Las Cruces, NM, USA

and Institute of Physics, CAS, Prague, CZR (Room 335)

zollner@nmsu.edu or zollner@fzu.cz

These lectures were supported by

- European Union, European Structural and Investment Funds (ESIF)
- Czech Ministry of Education, Youth, and Sports (MEYS), Project IOP Researchers Mobility – CZ.02.2.69/0.0/0.0/0008215

Thanks to Dr. Dejneka and his department at FZU.

EUROPEAN UNION
European Structural and Investment Funds
Operational Programme Research,
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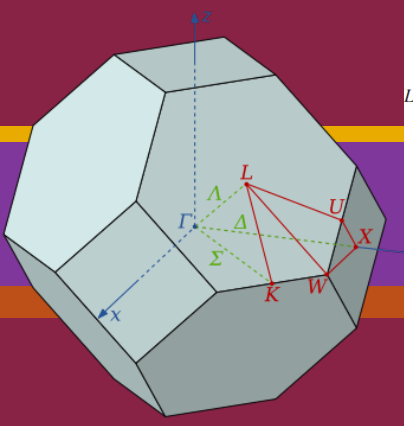
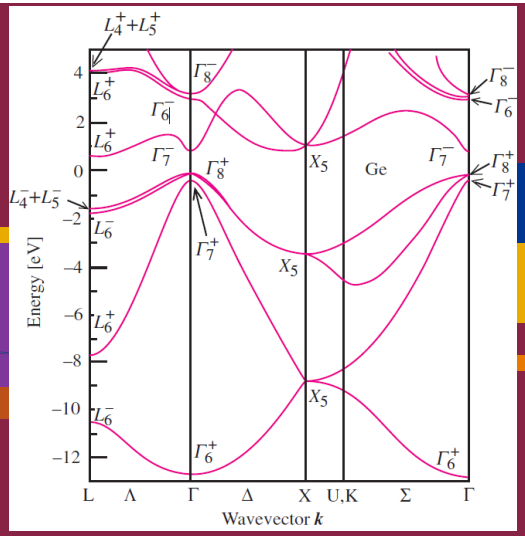
NSF: DMR-1505172

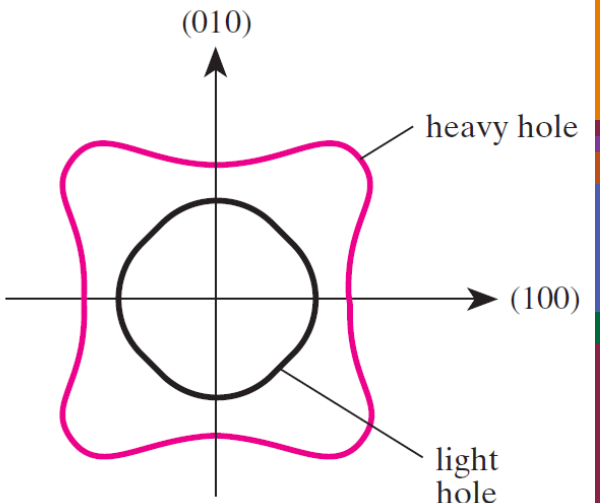
Optical Properties of Solids: Lecture 7+8

Electronic Band Structure
Direct and indirect band gaps
Empty lattice, pseudopotential, k.p band structures

Optical interband transitions, Fermi's Golden Rule
Absorption coefficient for direct and indirect gaps
Tauc plot
Van Hove singularities







References: Band Structure and Optical Properties

Solid-State Theory and Semiconductor Band Structures:

- Mark Fox, *Optical Properties of Solids*
- Ashcroft and Mermin, Solid-State Physics
- Yu and Cardona, Fundamentals of Semiconductors
- Dresselhaus/Dresselhaus/Cronin/Gomes, Solid State Properties
- Cohen and Chelikowsky, Electronic Structure and Optical Properties
- Klingshirn, Semiconductor Optics
- Grundmann, Physics of Semiconductors
- Ioffe Institute web site: NSM Archive
  http://www.ioffe.ru/SVA/NSM/Semicond/index.html

Outline

Band structure and Bloch's theorem
Examples: Si, Ge, Al, Cu, $SrTiO_3$
Free-electron approximation
Nearly free electron gas
Empirical and ab initio pseudopotential methods
k.p theory band structure method
Effective masses, valence band warping, Luttinger parameters

Band Structure: Where did this come from?

Crystal symmetry: **Translational + point group symmetry**.

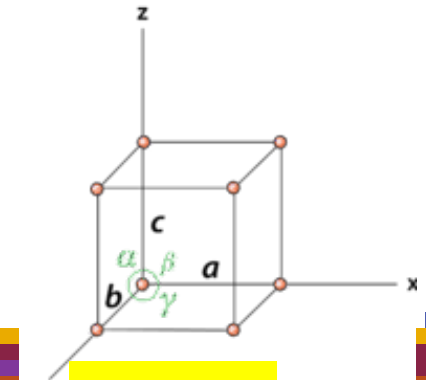
Translational symmetry results in **Bloch's Theorem.**

$$\vec{T}\psi(\vec{r}) = \psi\left(\vec{r}+\vec{T}\right) = e^{i\vec{k}\cdot\vec{T}}\psi(\vec{r})$$

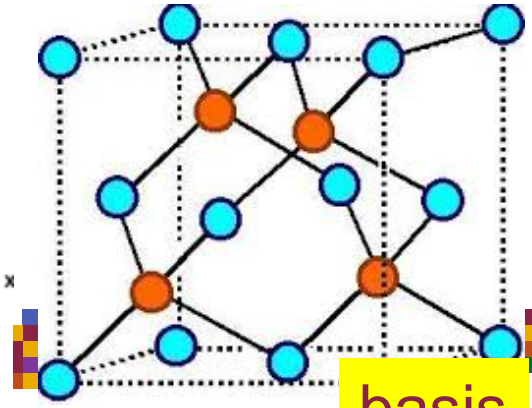
$$\psi(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}u_{n,\vec{k}}(\vec{r})$$

Representations of cyclic groups are one-dimensional generated by primitive lattice vectors. The characters are the roots of unity.

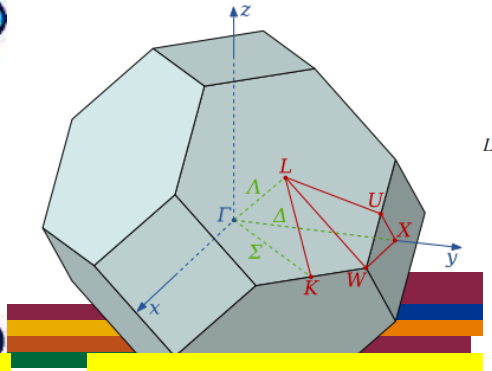
Energy and wave vector are good quantum numbers.
For each **k**, we label the bands from lower to higher energies.
This results in band structure $E_n(\mathbf{k})$, for **k** in Brillouin zone.



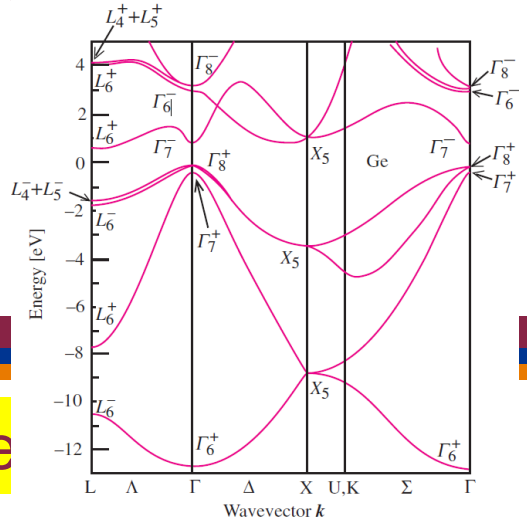
lattice



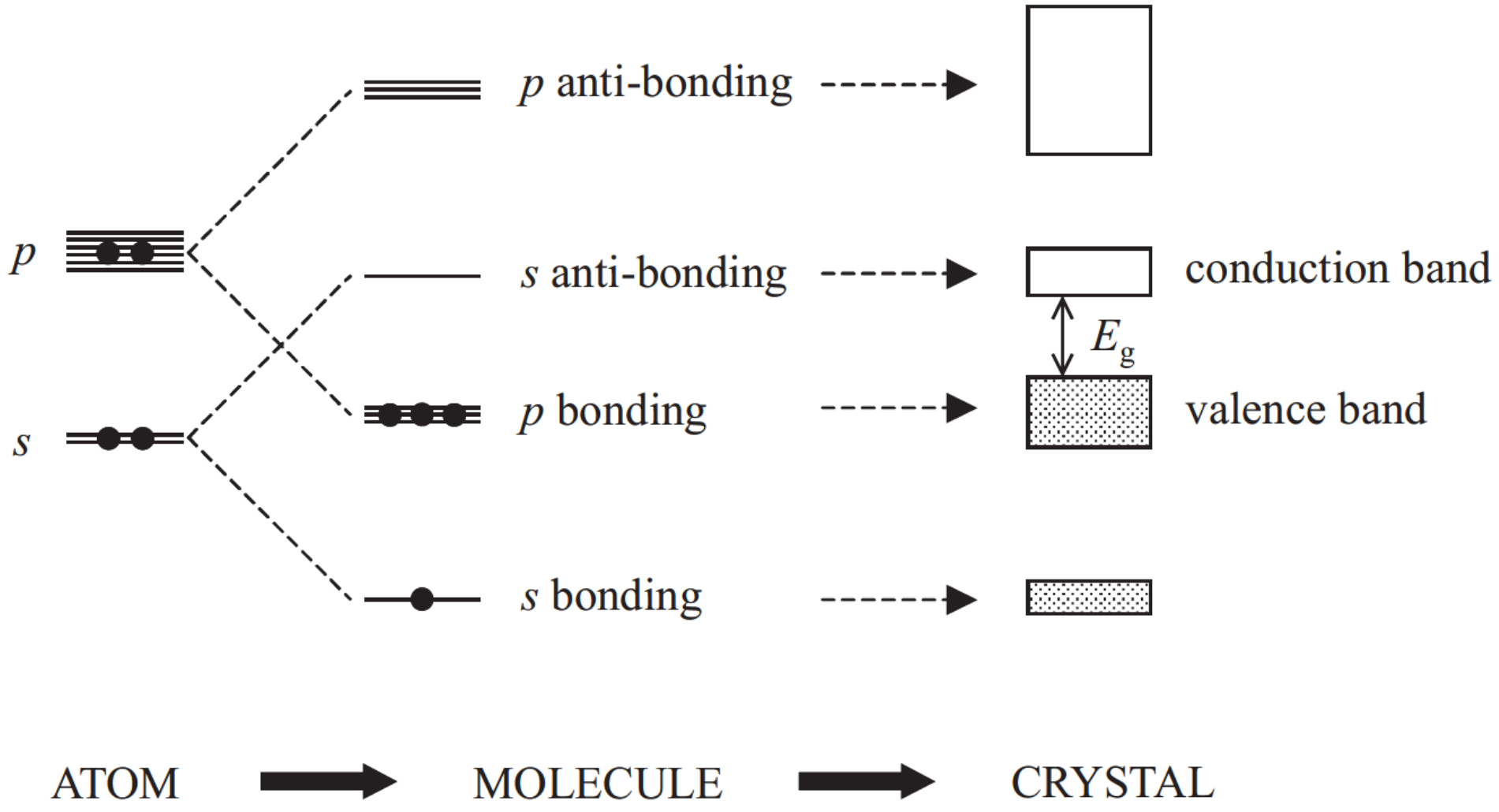
basis



Brillouin zone



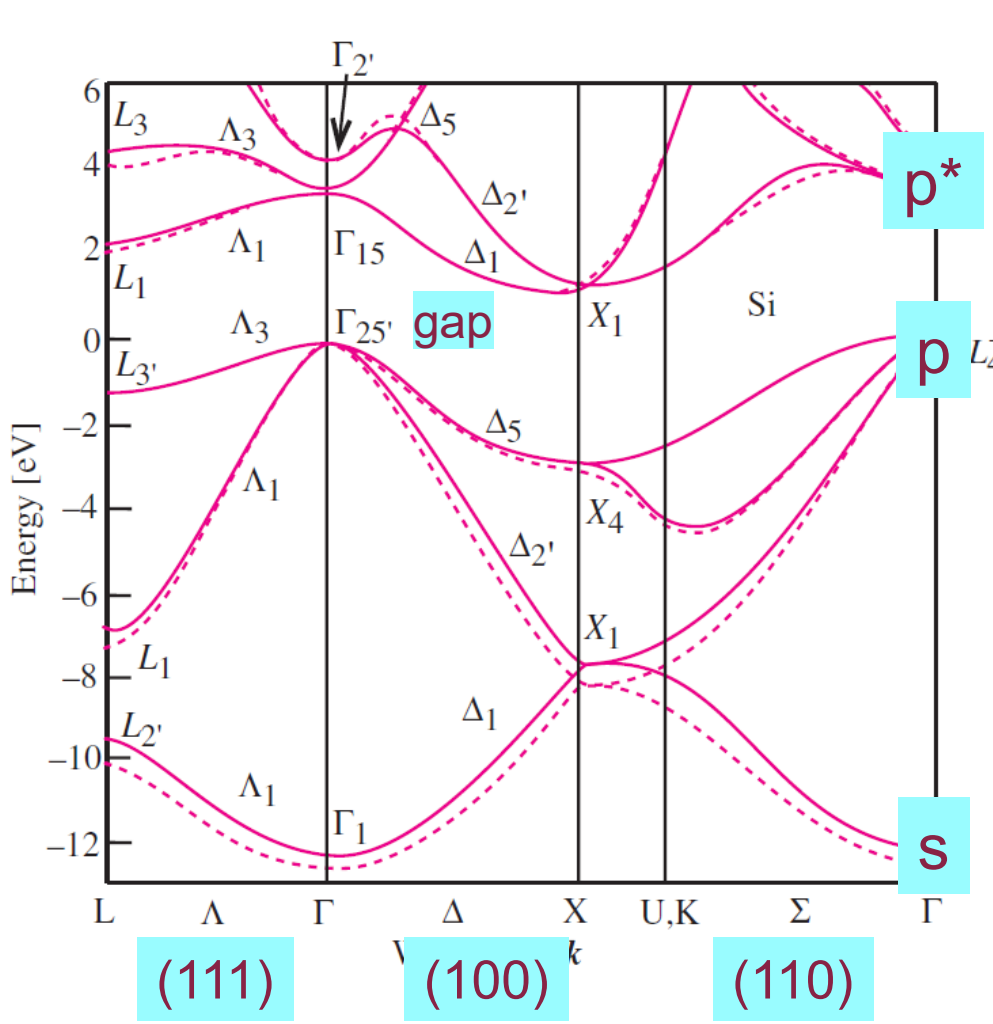
Band Structure: Where did this come from?

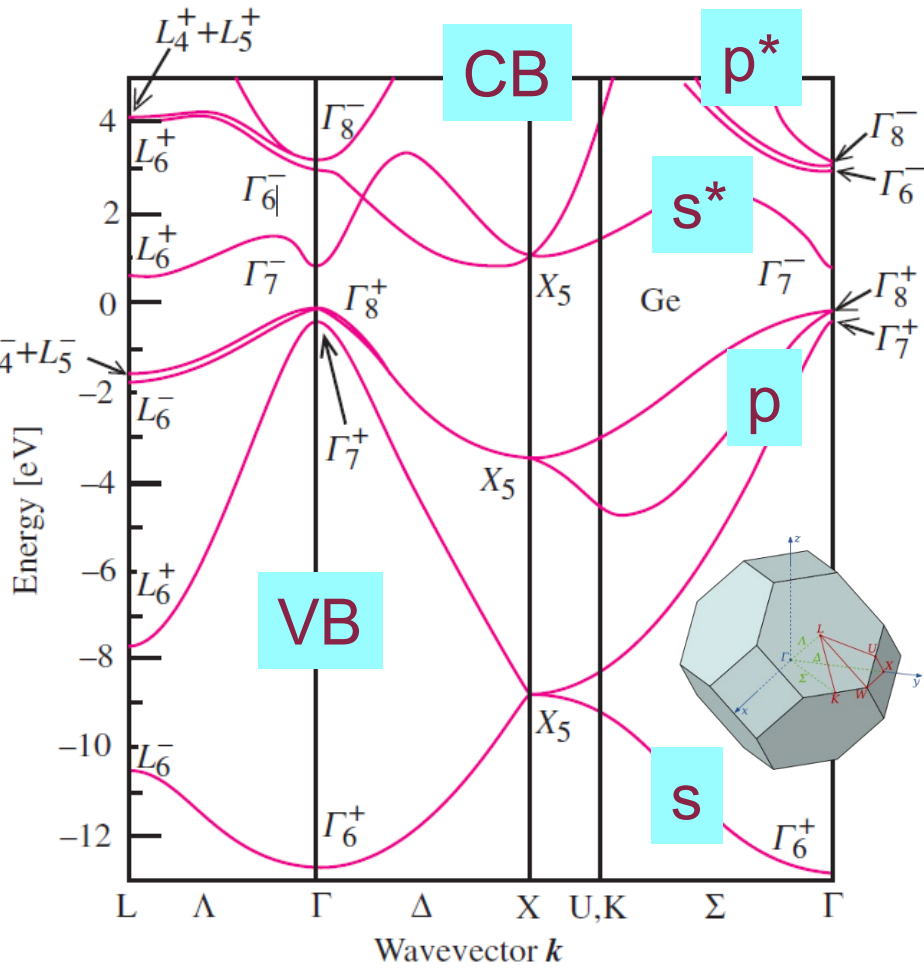


Works well for Ge, GaAs, etc.

Fox, Chapter 3

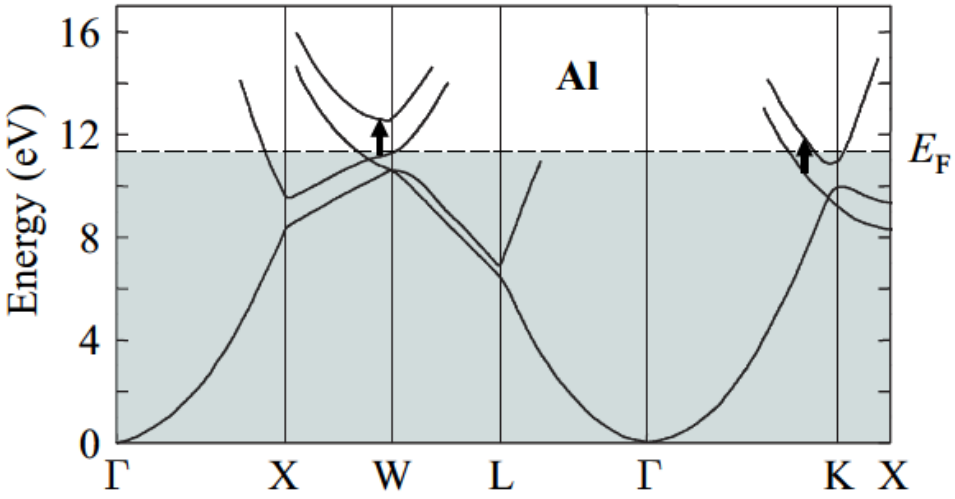
Examples of Band Structures: Si and Ge

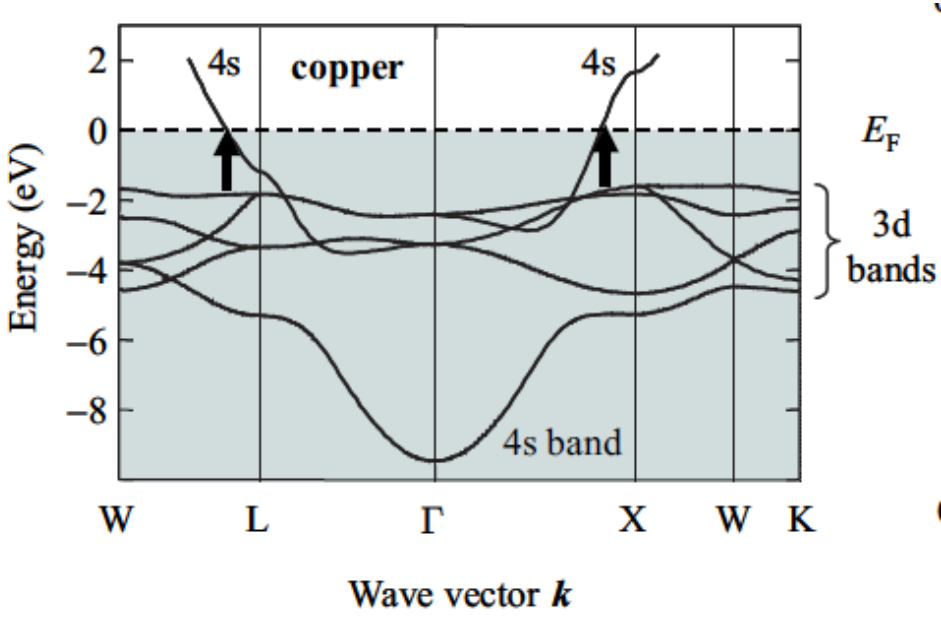




Total Energy: E=K+V, K=$\mathbf{p}^2/2m$, $\mathbf{p}=0$ corresponds to Γ-point in BZ.
Four valence electrons per atom: $3s^2$, $3p^2$ (8 e^- per cell)
Symmetry labels are representations from the point group.

Examples of Band Structures: Al and Cu

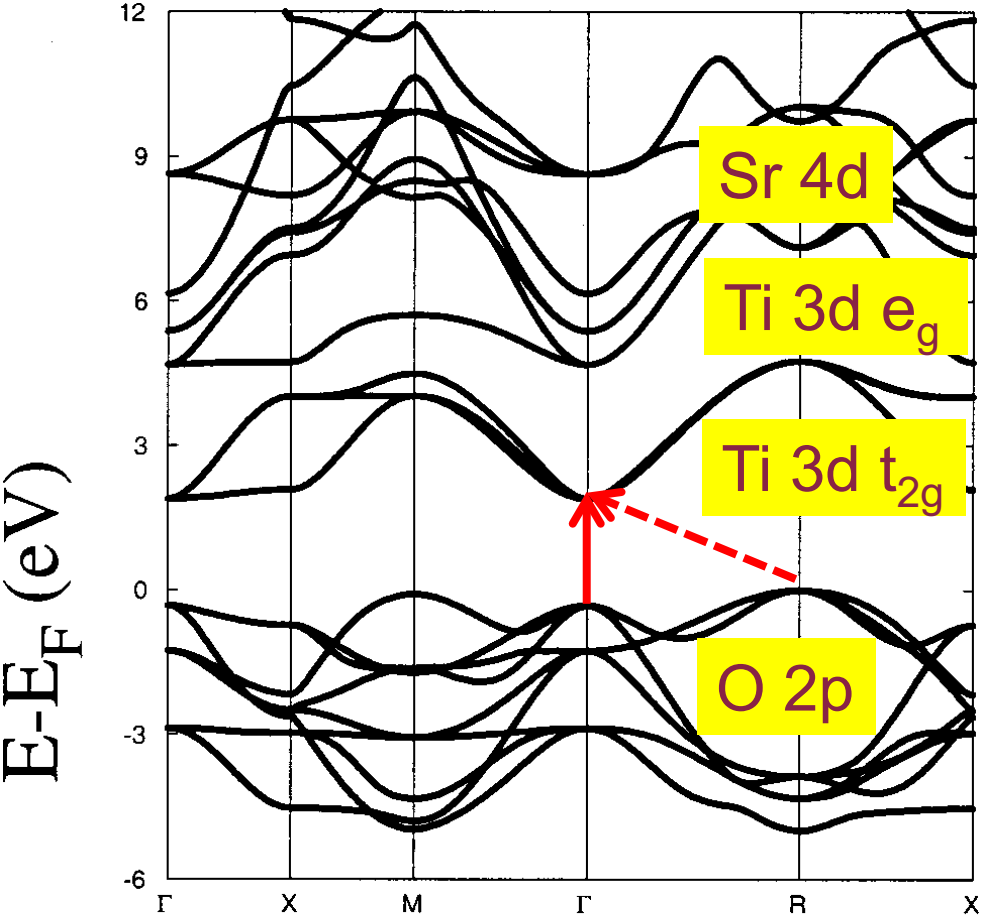


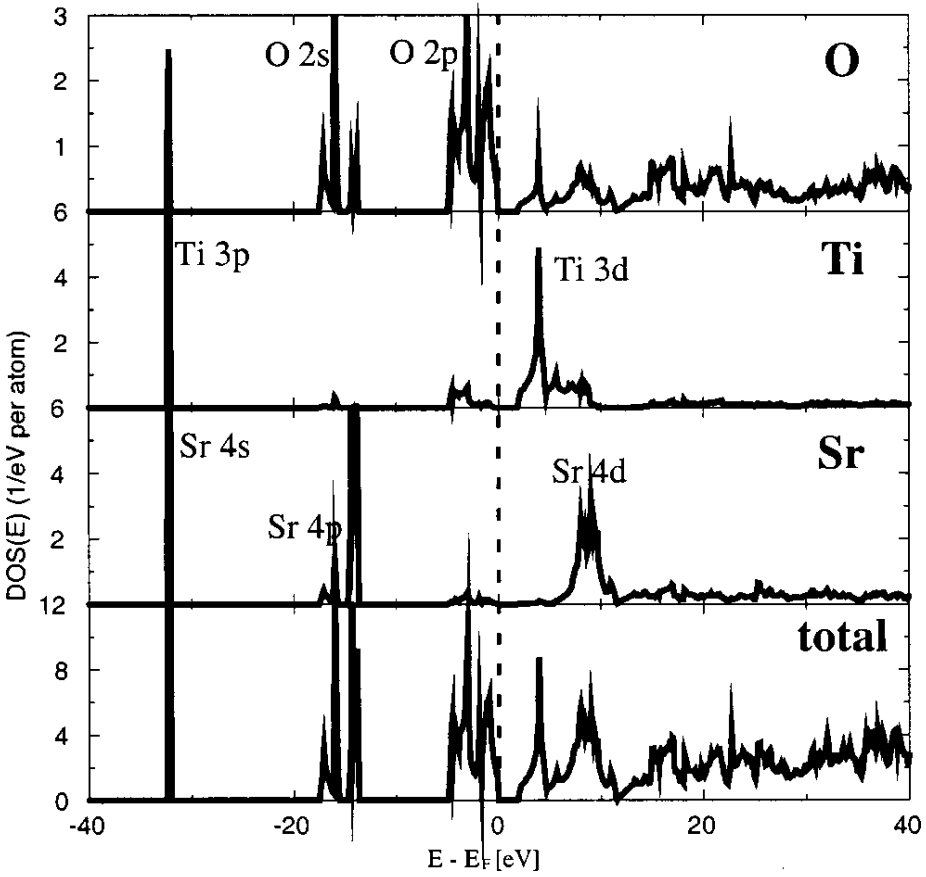


Three valence electrons:
$3s^2$, $3p^1$
No d-electrons.
3p band only half full.
(This must be a metal).

Noble metal Cu, Ag, Au:
s-band half full (metal)
d-bands completely full.
Not ferromagnetic
(paired d-electron spins).

Examples of Band Structures: $SrTiO_3$



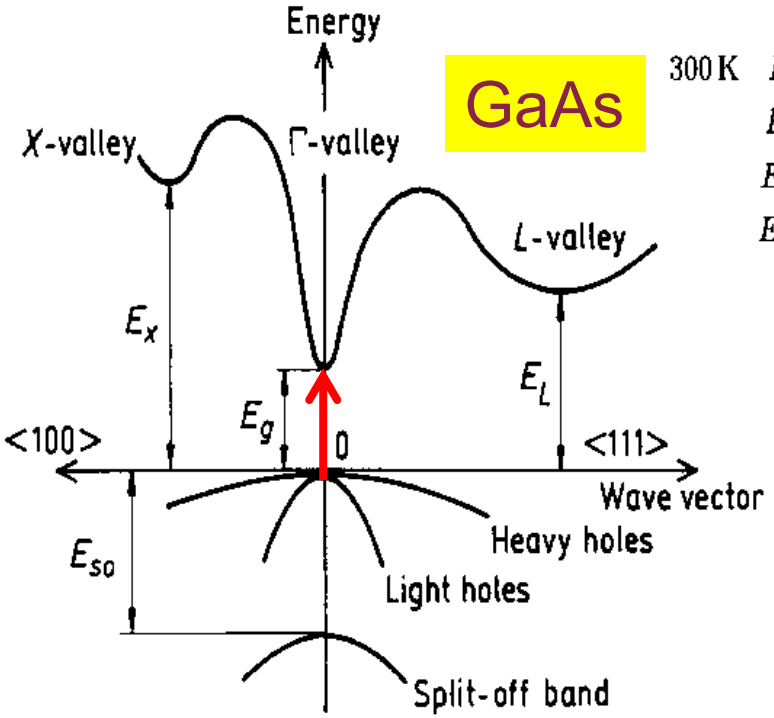


LDA underestimates gap (need GW).
Hybrid functionals for d-electrons (LDA+U).
Direct/indirect transitions.

Projected density of states.

Benthem JAP **90**, 6156 (2001)

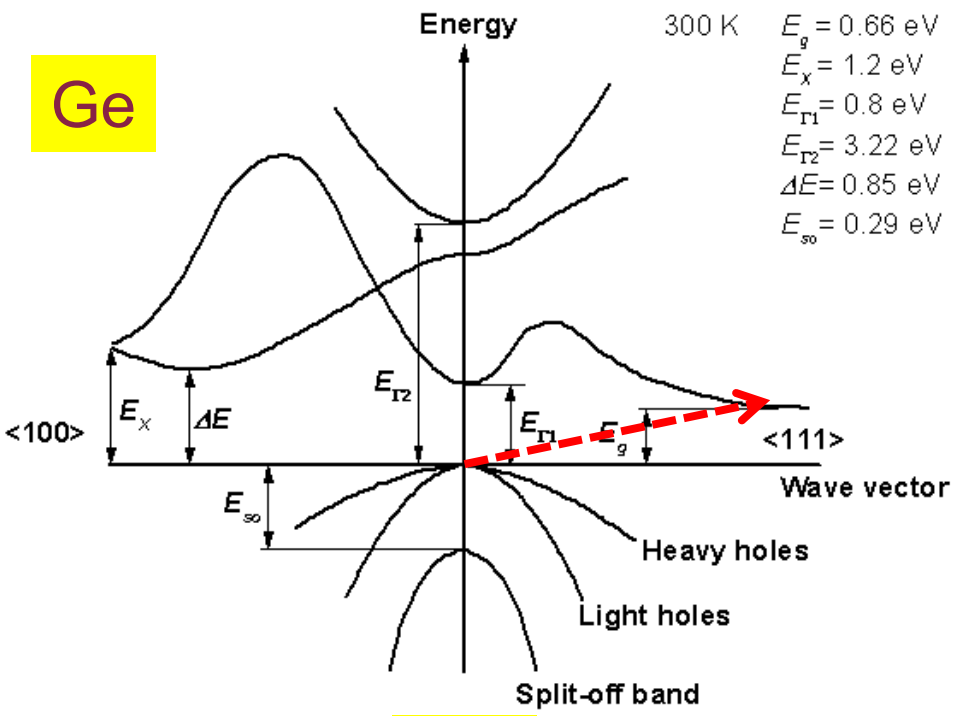
Direct and indirect transitions



GaAs

300 K $E_g = 1.42$ eV
$E_L = 1.71$ eV
$E_X = 1.90$ eV
$E_{so} = 0.34$ eV

k=0



Ge

300 K
$E_g = 0.66$ eV
$E_X = 1.2$ eV
$E_{Γ1} = 0.8$ eV
$E_{Γ2} = 3.22$ eV
$\Delta E = 0.85$ eV
$E_{so} = 0.29$ eV

k=0

Direct transition:

Initial and final electron state have **same** wave vector.

Indirect transition:

Initial and final electron state have **different** wave vector.

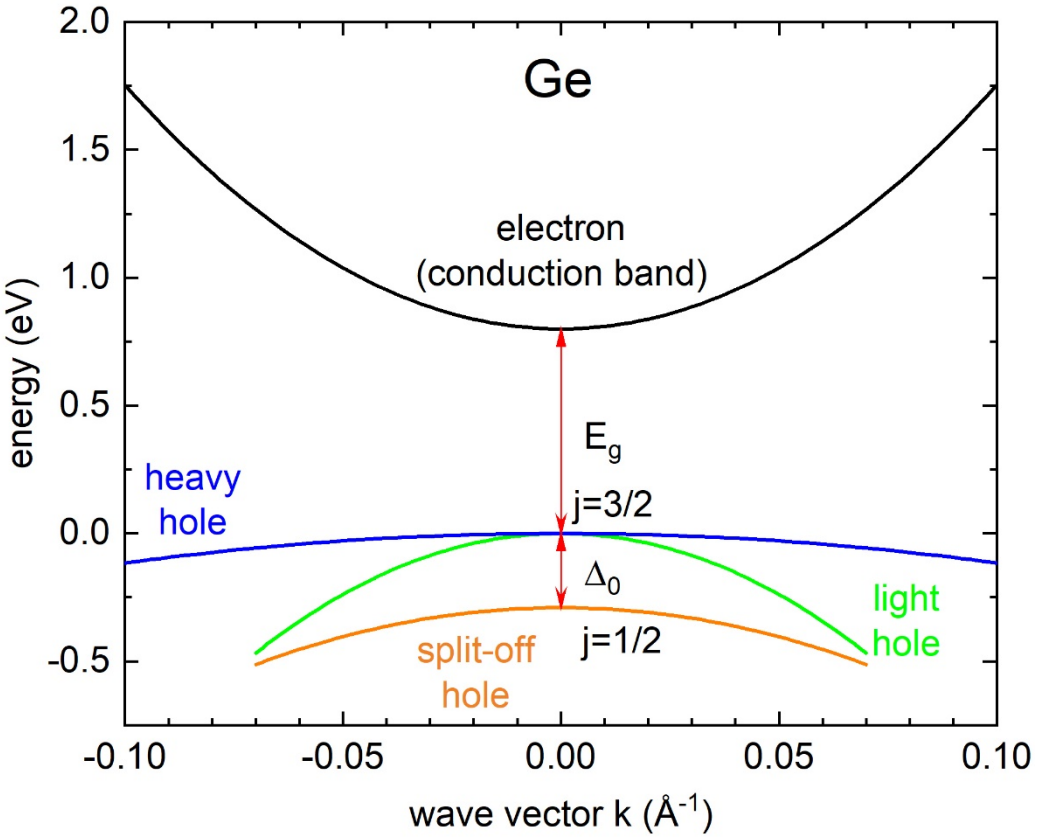
http://www.ioffe.ru/SVA/NSM/Semicond/index.html

Free-electron approximation (empty lattice: V=0)

$$H = T + U$$

Ignore potential energy (U=0)

$$H = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 k^2}{2\boldsymbol{m}^* m_0}$$



$$E_e = E_g + \frac{\hbar^2 k^2}{2\boldsymbol{m_e} m_0}$$

$$E_{hh} = -\frac{\hbar^2 k^2}{2\boldsymbol{m_{hh}} m_0}$$

$$E_{lh} = -\frac{\hbar^2 k^2}{2\boldsymbol{m_{lh}} m_0}$$

$$E_{so} = -\Delta_0 - \frac{\hbar^2 k^2}{2\boldsymbol{m_{so}} m_0}$$

$$(m_{ij})^{-1} = \frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k_i \partial k_j}$$

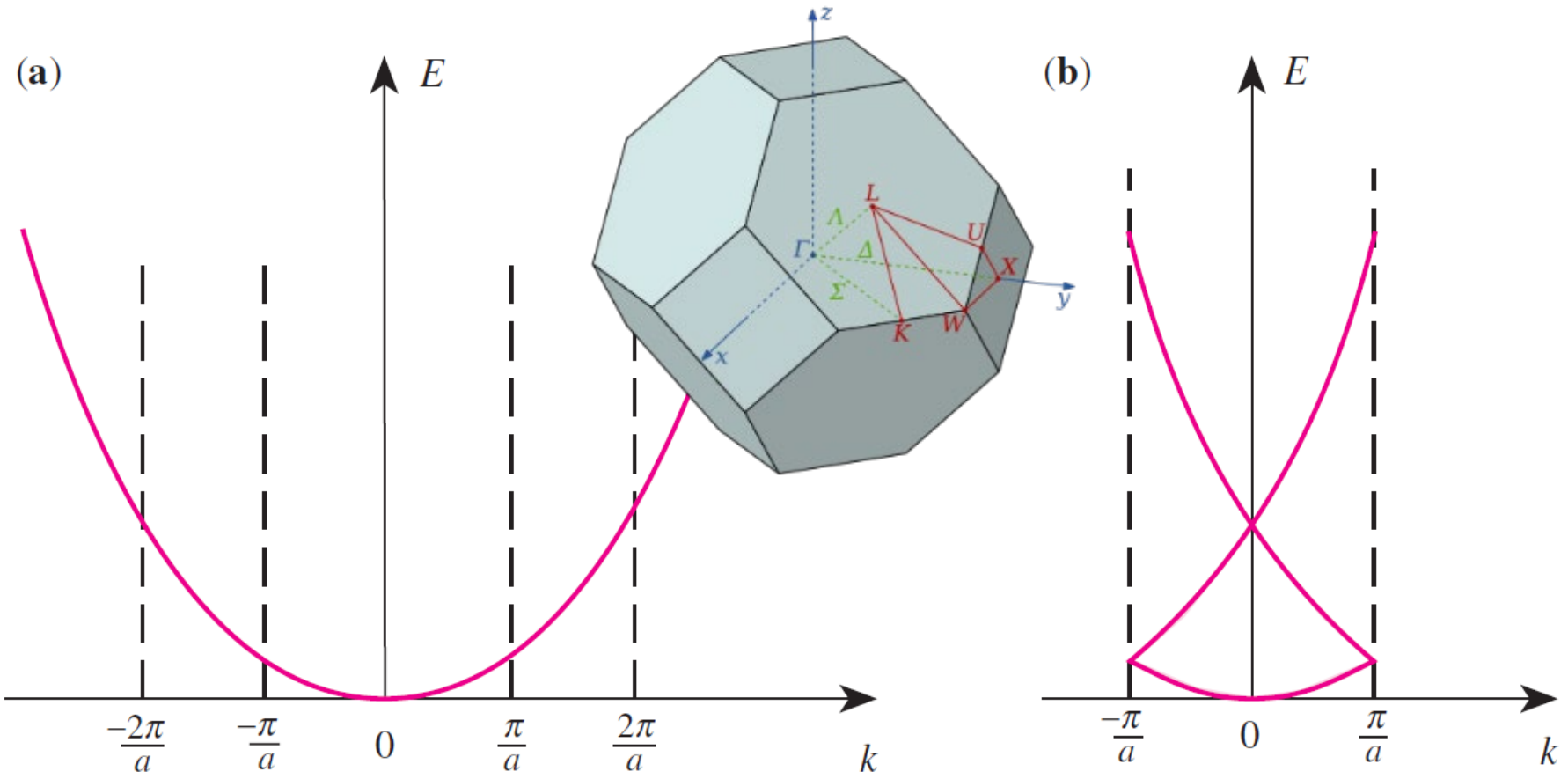
Effective mass $\boldsymbol{m}^*$

Effective mass tensor

Free particle: Plane wave

Yu & Cardona, Fundamentals of Semiconductors

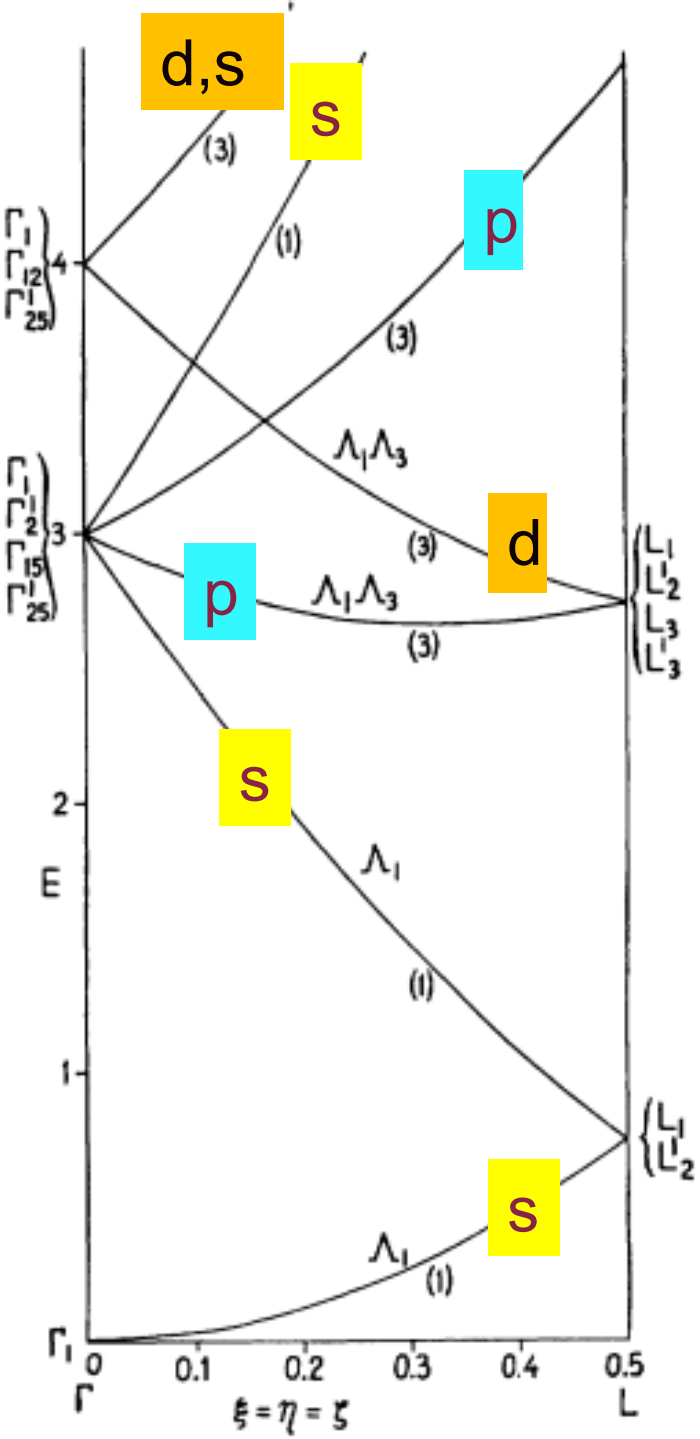
Free-electron approximation (empty lattice: V=0)

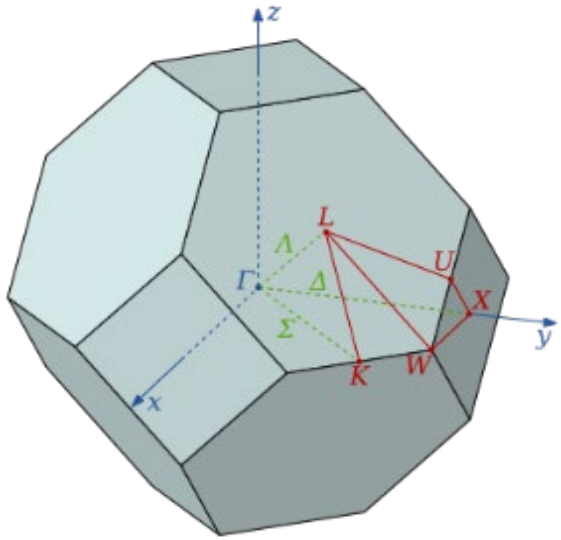


Bands are folded at edges of Brillouin zone.

Yu & Cardona, Fundamentals of Semiconductors
H. Jones, Theory of Brillouin Zones (1975)

Free-electron approximation for FCC lattice





Bands are folded at edges of Brillouin zone.

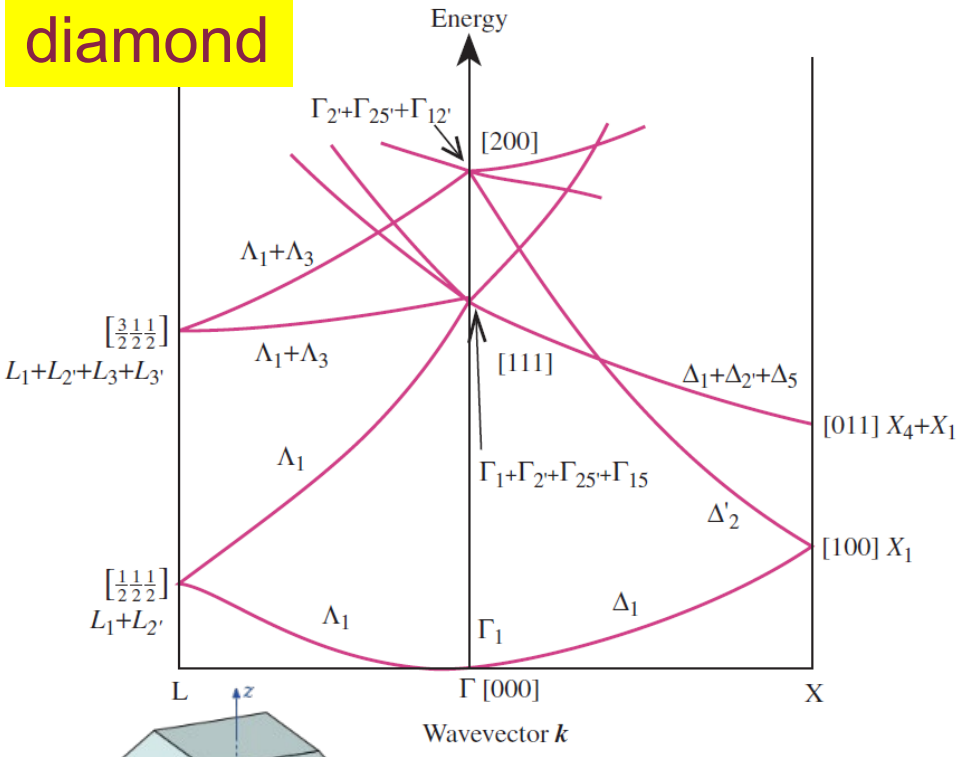
Wave functions are plane waves (calculated matrix elements).

Note point group symmetry notations.

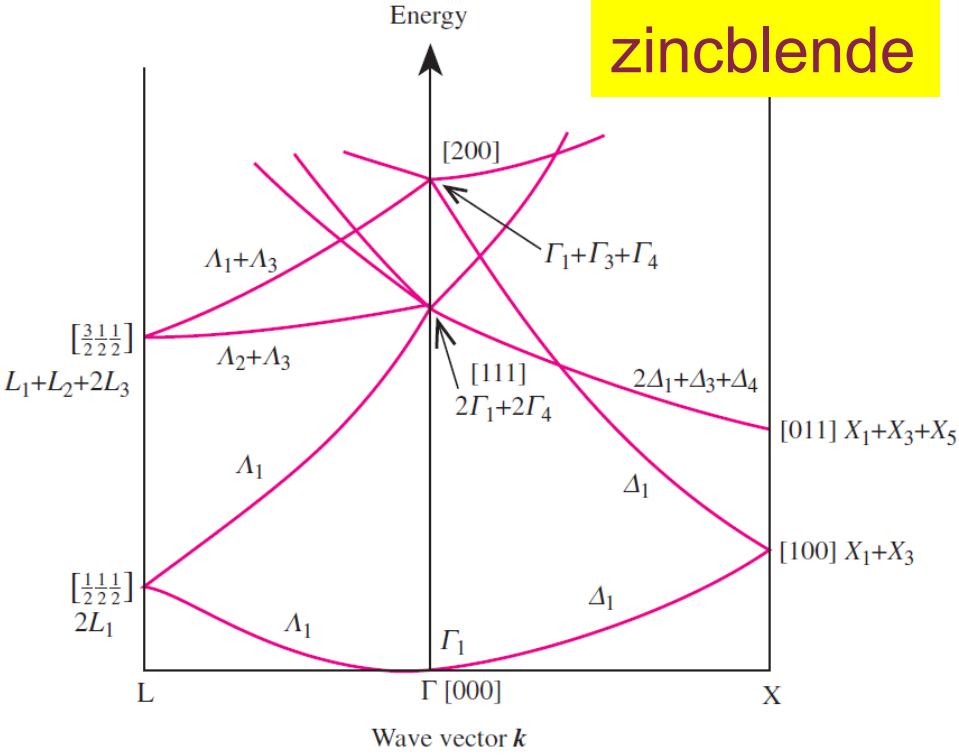
Yu & Cardona, Fundamentals of Semiconductors
H. Jones, Theory of Brillouin Zones (1975)

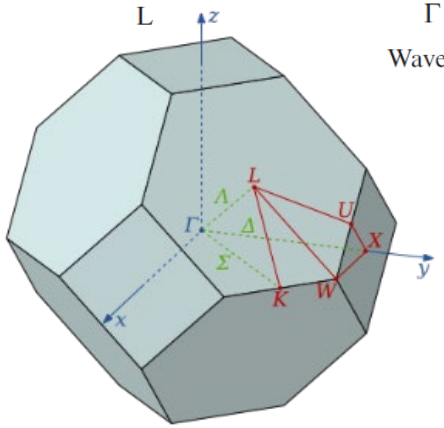
Free-electron approximation for FCC lattice

diamond



zincblende



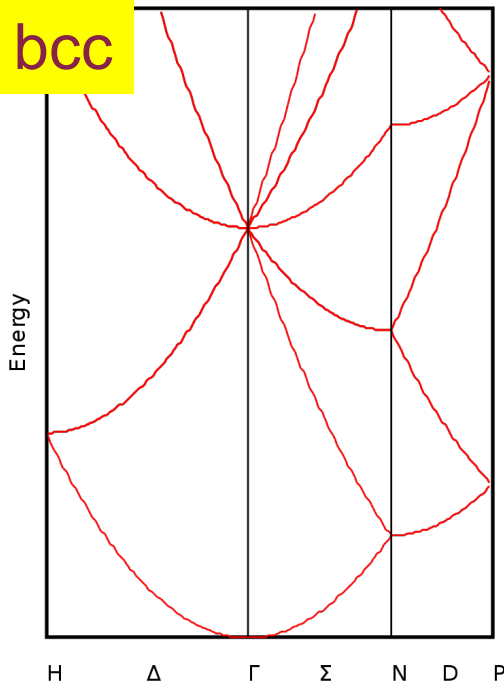


Bands are folded at edges of Brillouin zone.
Wave functions are plane waves related to RLV **K**
(calculate matrix elements).
Note point group symmetry notations.
No crystal potential: Lots of degeneracies

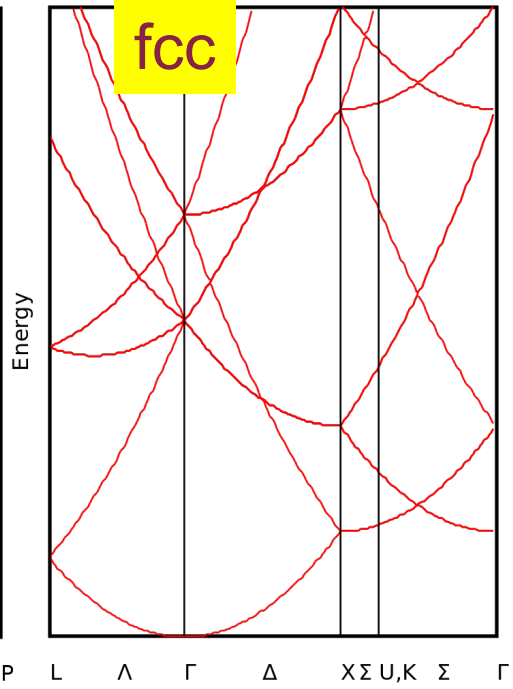
Yu & Cardona, Fundamentals of Semiconductors

Free-electron approximation: bcc, fcc, hcp lattices

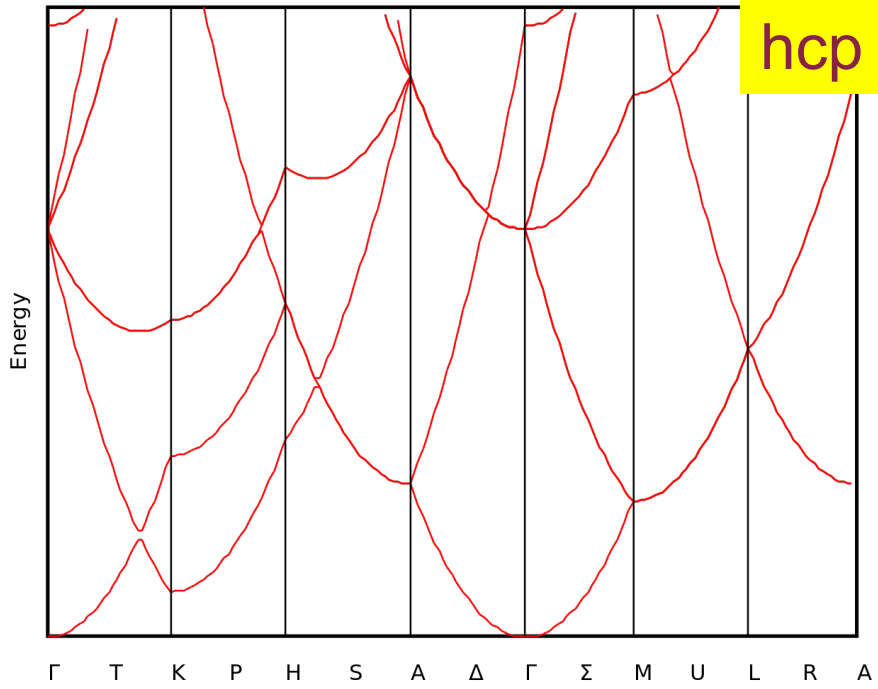
bcc

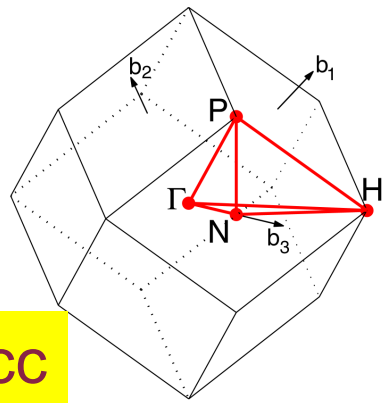


fcc

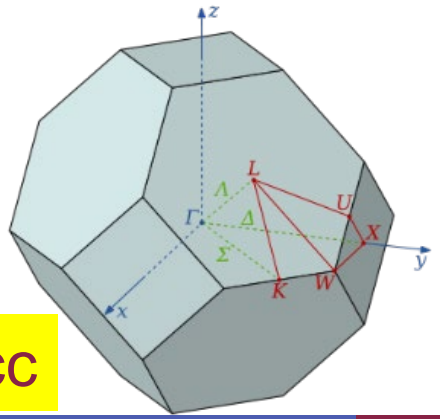


hcp

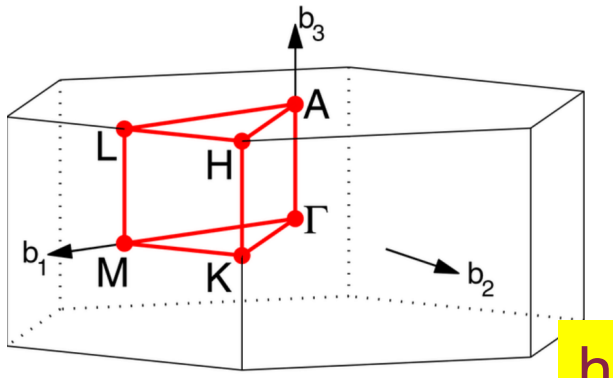




bcc



fcc



hcp

Wikipedia (empty lattice approximation)

Nearly free electron gas (weak potential)

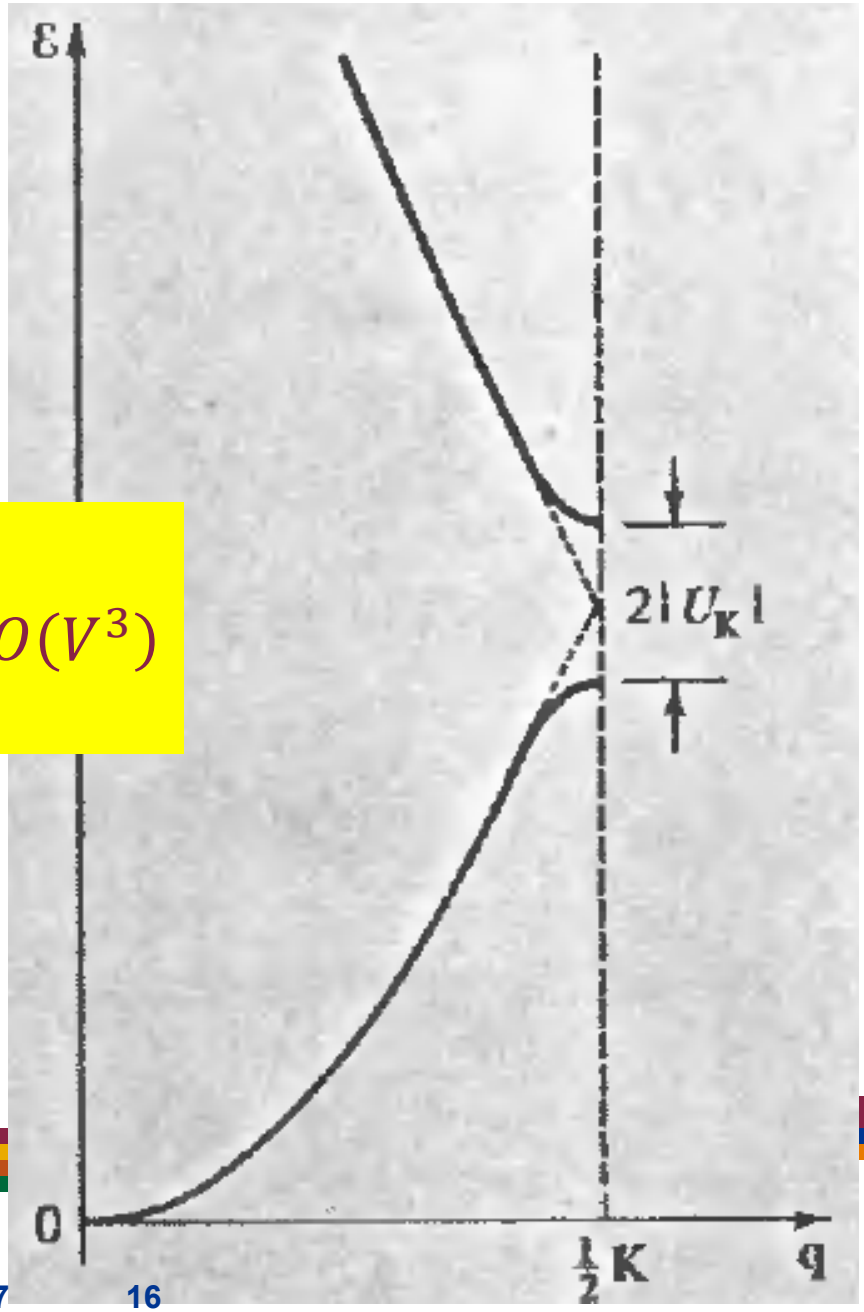
$$H = T + U$$

Assume that U is very small.

Non-degenerate states are not affected much (second order in U).
Bands repel each other.

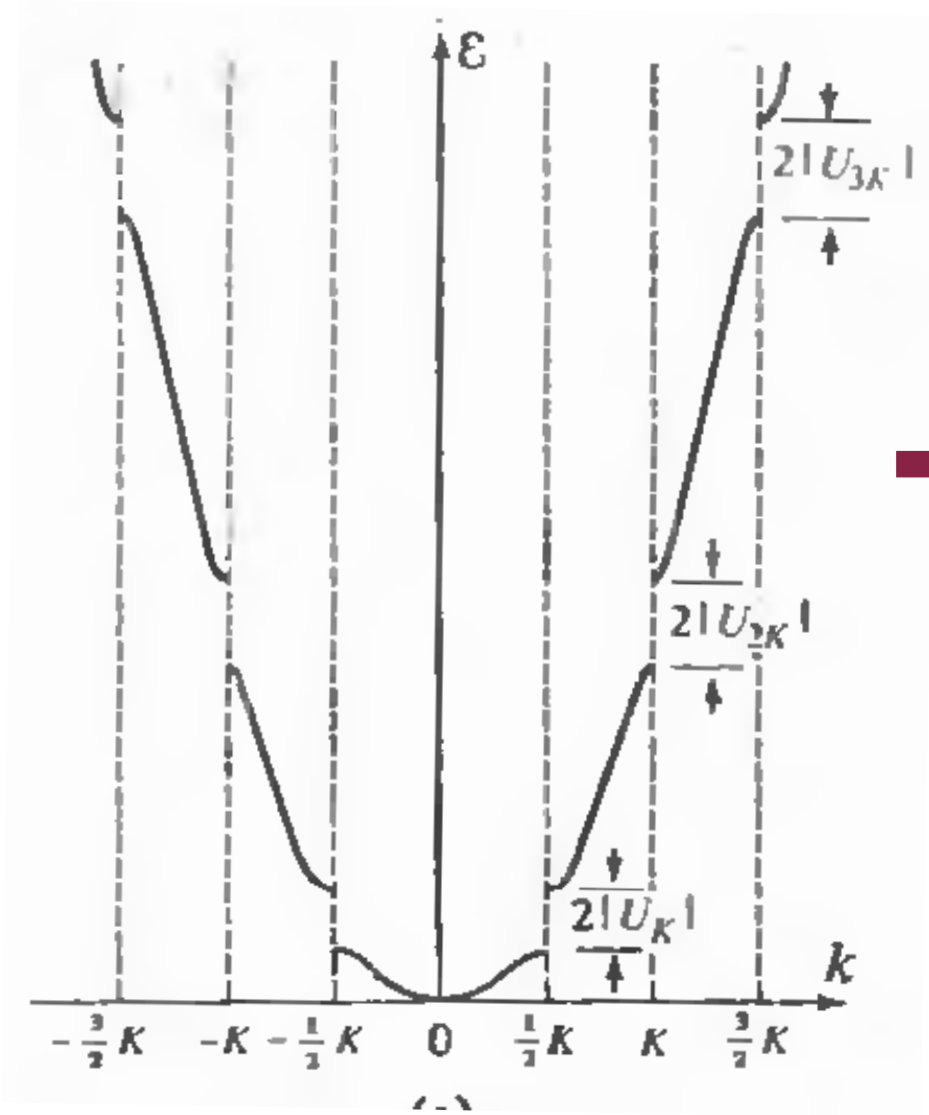
$$E(\vec{k}) = E^0_{\vec{k}-\vec{K}_1} + \sum_{\vec{K}} \frac{\left|U_{\vec{K}-\vec{K}_1}\right|^2}{E^0_{\vec{k}-\vec{K}_1} - E^0_{\vec{k}-\vec{K}}} + O(V^3)$$

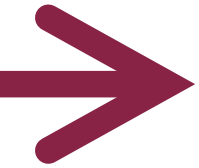
Degeneracies are lifted.
Gaps open, especially near the BZ boundary.



Ashcroft&Mermin, Chapter 9

Nearly free electron gas (weak potential)



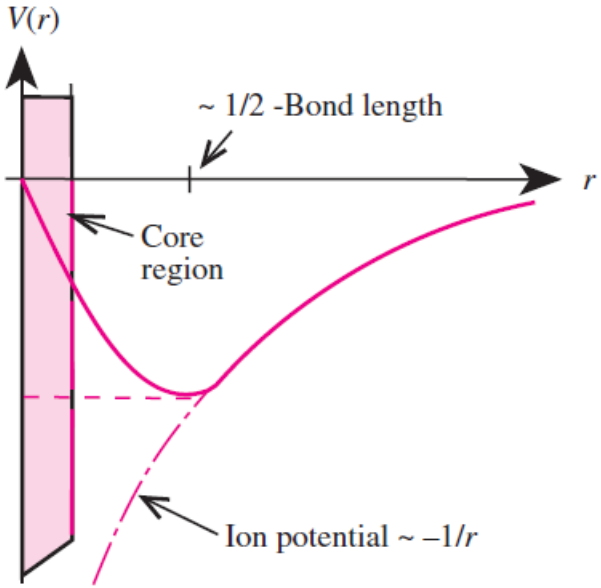


Band gap

Ashcroft&Mermin, Chapter 9

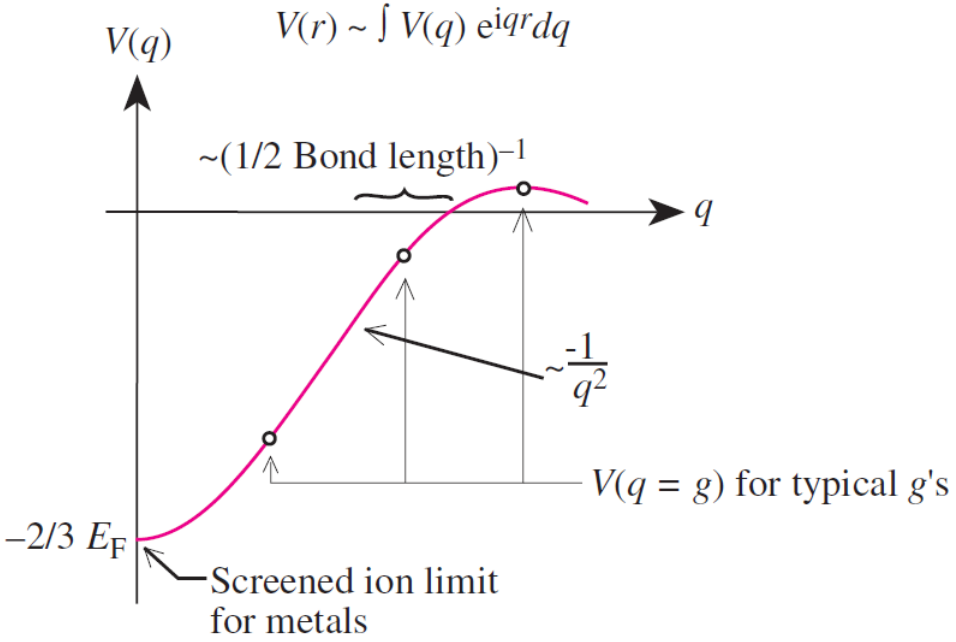
Crystal potential as pseudopotential

Real-space pseudopotential



Coulomb potential diverges for r=0.
Replace with “soft-core” pseudopotential.

Reciprocal-space pseudopotential



Only need to know V(g) for a few points.
Calculate band structure with empirical pseudopotential (EPM) method.
Requires diagonalization of 59x59 matrix.

Yu & Cardona, Fundamentals of Semiconductors

Crystal potential as pseudopotential

Empirical pseudopotential method

$$V_g \downarrow$$

$$V(\boldsymbol{r}) = \sum_g V_g \exp(-i\mathbf{g}\cdot\boldsymbol{r}) \downarrow$$

$$H = (p^2/2m) + V(\boldsymbol{r})$$

Solve $H\psi_k(\boldsymbol{r}) = E_k\psi_k(\boldsymbol{r})$ to obtain $\psi_k(\boldsymbol{r})$ and E_k $\downarrow$

Calculate reflectivity, density of states, etc., and compare with experiments $\downarrow$

Alter V_g if agreement between theory and experiment is not satisfactory.

Self-consistent pseudopotential method

Choose $V(r)$ $\downarrow$

Solve $(H + V)\psi = E\psi$ $\downarrow$

Calculate charge density $\varrho = \psi^*\psi$ $\downarrow$

Solve $\nabla^2 V_{\text{Hartree}} = 4\pi\varrho\left(\frac{1}{4\pi\varepsilon_0}\right)$ $\downarrow$

Calculate $V_{\text{xc}} = f[\varrho(r)]$ $\downarrow$

$V_{\text{sc}} = V_{\text{Hartree}} + V_{\text{xc}}$ $\downarrow$

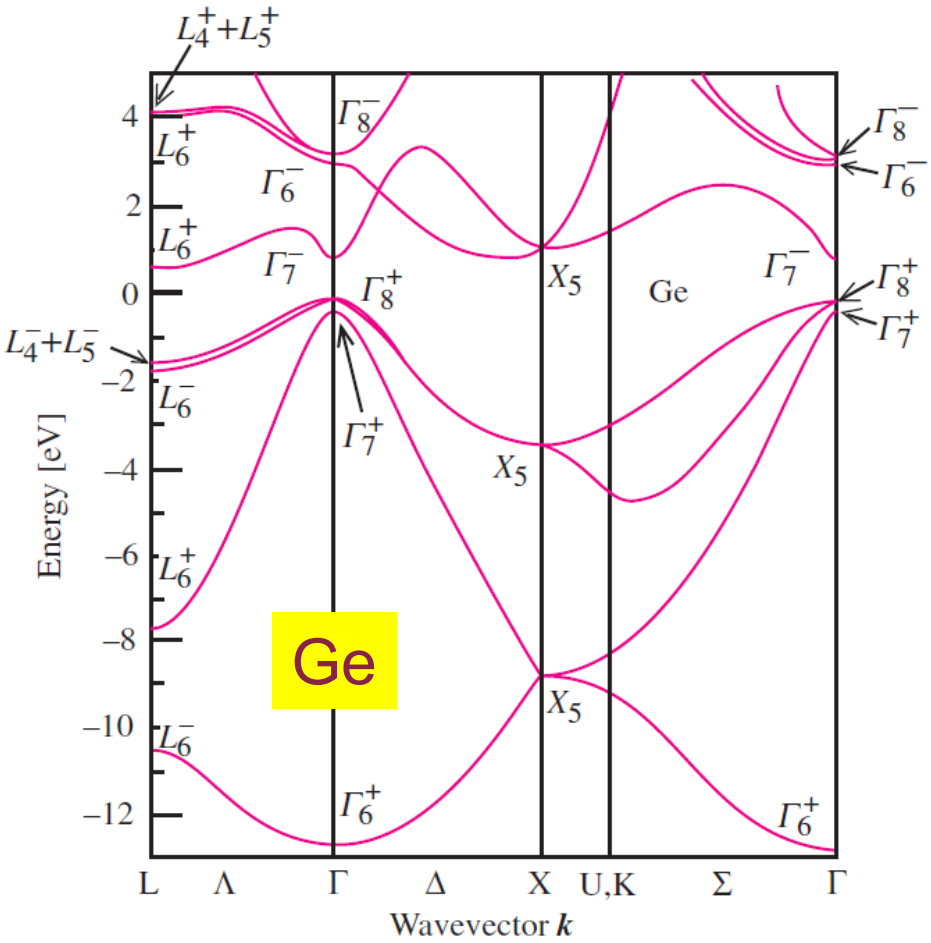
Model structure $V_{\text{ion}} \rightarrow V = V_{\text{sc}} + V_{\text{ion}}$

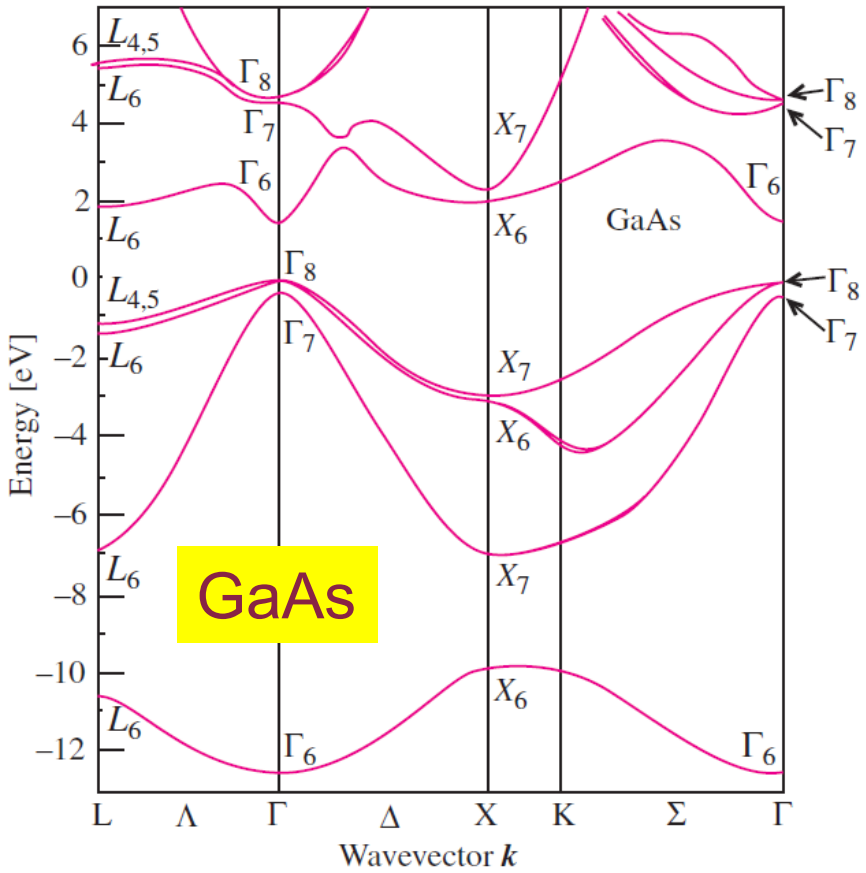
Guess V(g)
Calculate band structure
Compare with experimental results.
Adjust V(g) until good agreement.
Single-electron equation.
Diagonalization of a matrix works for s- and p-electrons (not d-electrons).

Start with atomic pseudopotential V
Calculate band structure
Calculate charge density ρ
Include many-body effects (LDA)
Replace V and start over.
No experimental input needed.

Yu & Cardona, Fundamentals of Semiconductors
Cohen & Bergstresser, Phys. Rev. **141**, 789 (1966).

Pseudopotential (EPM) band structures for Ge, GaAs

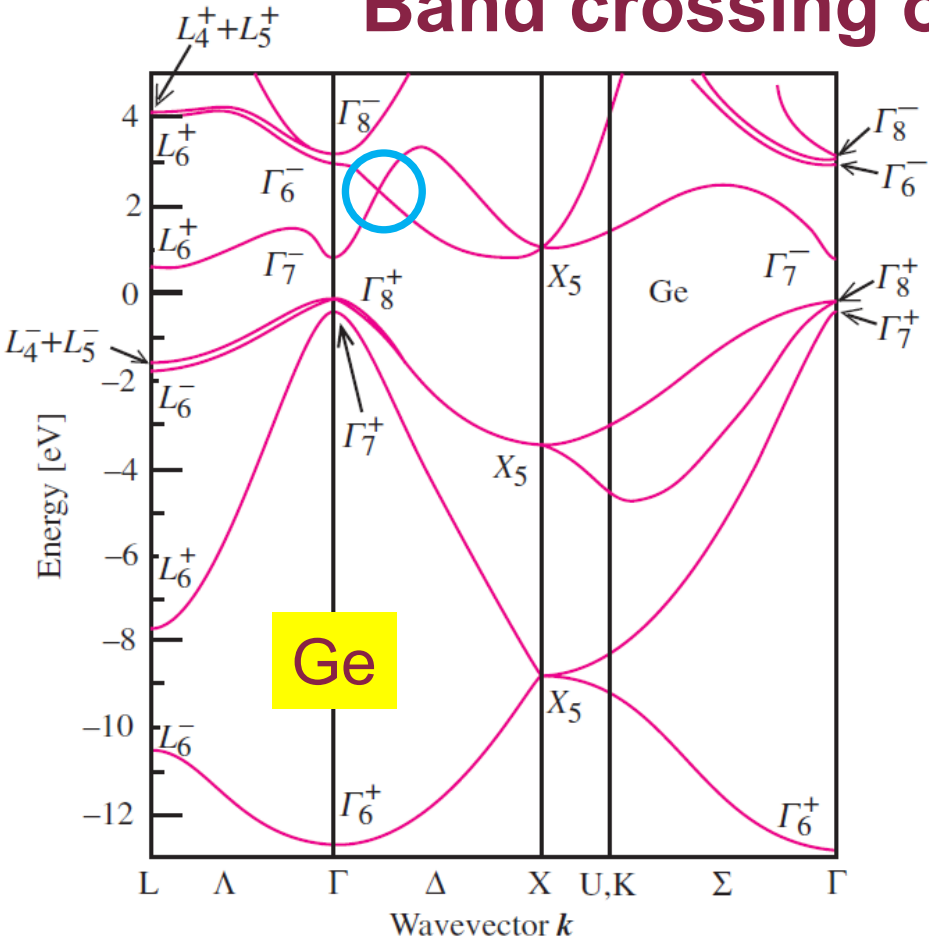


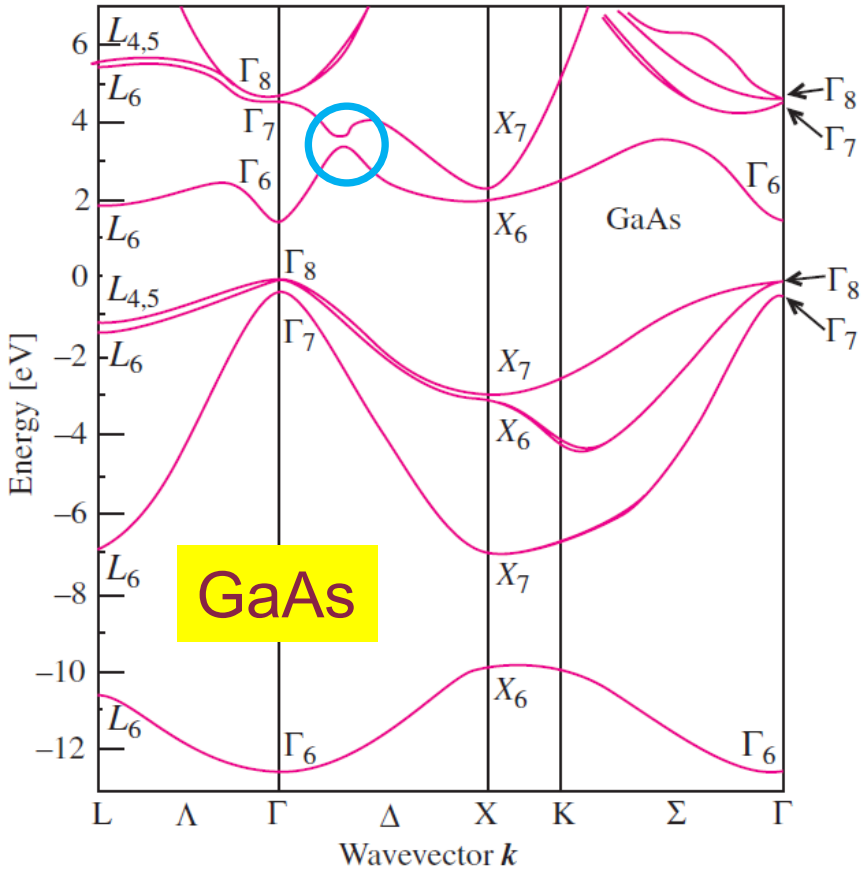


Compare with empty lattice results:
Crystal potential opens a band gap.
Bands are flat at BZ edges.

Chelikowsky & Cohen, PRB 14 556 (1976)

Band crossing or anti-crossing





Bands cross: different symmetries.
Dirac point: Linear dependence on k
Inversion symmetry leads to crossing.

Bands repel: same symmetry.
Anti-crossing due to interactions.
No degeneracy at the X-point.

k·p theory (band structure method)

Schrödinger equation

$$H\Phi_{n\vec{k}} = \left(\frac{\vec{p}^2}{2m} + V\right)\Phi_{n\vec{k}} = E_{n\vec{k}}\Phi_{n\vec{k}}$$

Use Bloch's theorem:

$$\Phi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}u_{n\vec{k}}(\vec{r})$$

Product rule

$$(fg)'' = f''g + 2f'g' + fg''$$

$$\left(\frac{\vec{p}^2}{2m} + \frac{\hbar^2\vec{k}^2}{\boldsymbol{2m}} + \frac{\hbar\vec{k}\cdot\vec{p}}{\boldsymbol{m}} + V\right)u_{n\vec{k}} = E_{n\vec{k}}u_{n\vec{k}}$$

Solve equation for **k**=0.

Then treat red terms in perturbation theory.

Works very well for semiconductors with local V(**r**) potentials.

Yu & Cardona, Fundamentals of Semiconductors

k·p theory: Effective mass of a non-generate band

$$\left(\frac{\vec{p}^2}{2m}+\frac{\hbar^2\vec{k}^2}{2m}+\frac{\hbar\vec{k}\cdot\vec{p}}{m}+V\right)u_{n\vec{k}}=E_{n\vec{k}}u_{n\vec{k}}$$

Solve for **k**=0 (at Γ). Linear terms in **k** vanish (extremum).
Treat red terms in perturbation theory (up to second order).

$$u_{n\vec{k}}=u_{n\Gamma}+\frac{\hbar}{m}\sum_{n'\neq n}\frac{\langle u_{n\Gamma}|\vec{k}\cdot\vec{p}|u_{n'\Gamma}\rangle}{E_{n\Gamma}-E_{n'\Gamma}}u_{n'\Gamma}$$

$$E_{n\vec{k}}=E_{n\Gamma}+\frac{\hbar^2k^2}{2m}+\frac{\hbar^2}{m^2}\sum_{n'\neq n}\frac{\left|\langle u_{n\Gamma}|\vec{k}\cdot\vec{p}|u_{n'\Gamma}\rangle\right|^2}{E_{n\Gamma}-E_{n'\Gamma}}=E_{n\Gamma}+\frac{\hbar^2k^2}{2m^*}$$

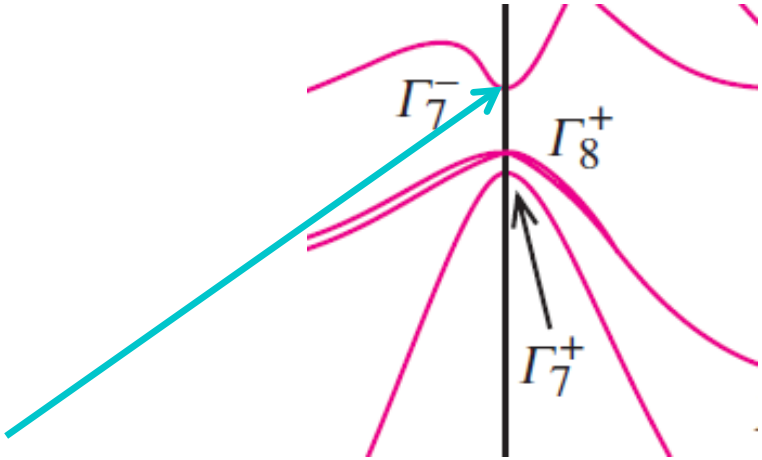
$$\frac{1}{m^*}=\frac{1}{m}+\frac{2}{m^2k^2}\sum_{n'\neq n}\frac{\left|\langle u_{n\Gamma}|\vec{k}\cdot\vec{p}|u_{n'\Gamma}\rangle\right|^2}{E_{n\Gamma}-E_{n'\Gamma}}$$

Effective mass comes from band-band interactions.

Yu & Cardona, Fundamentals of Semiconductors

k·p theory: Application to electron band at Γ

$$\frac{1}{m^*} = \frac{1}{m} + \frac{2}{m^2 k^2} \sum_{n' \neq n} \frac{\left|\langle u_{n\Gamma} | \vec{k} \cdot \vec{p} | u_{n'\Gamma} \rangle\right|^2}{E_{n\Gamma} - E_{n'\Gamma}}$$



Keep only the largest term:

$$\frac{1}{m_e^*} = \frac{1}{m_0} + \frac{2\left|\langle \Gamma_{1c} | \vec{k} \cdot \vec{p} | \Gamma'_{25v} \rangle\right|^2}{m_0^2 E_0 k^2} = \frac{1}{m_0} + \frac{2P^2}{m_0^2 E_0} \cong \frac{2P^2}{m_0^2 E_0}$$

$E_P = 2P^2/m_0$
$E_P \approx 20$ eV

Momentum matrix element: $iP = \langle X | p_x | \Gamma_1 \rangle = \langle Y | p_Y | \Gamma_1 \rangle = \langle Z | p_z | \Gamma_1 \rangle$

	Ge	GaN	GaAs	GaSb	InP	InAs	ZnS	ZnSe	ZnTe	CdTe
E_0 [eV]	0.89	3.44	1.55	0.81	1.34	0.45	3.80	2.82	2.39	1.59
m_c^*/m (exp)	0.041	0.17	0.067	0.047	0.073	0.026	0.20	0.134	0.124	0.093
m_c^*/m ((2.44))	0.04	0.17	0.078	0.04	0.067	0.023	0.16	0.14	0.12	0.08

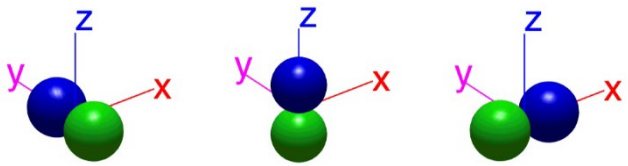
$m_e^* \propto E_0$

Yu & Cardona, Fundamentals of Semiconductors

k·p theory: Application to valence bands at Γ

Valence band maximum Γ_{25}': Spherical harmonics (L=1)

$$|lm_l\rangle = \begin{cases} |11\rangle = -(X+iY)/\sqrt{2} \\ |10\rangle = Z \\ |1{-}1\rangle = (X-iY)/\sqrt{2} \end{cases}$$



Include spin ½: J=L+S, j=1/2,3/2

$$|jm_j\rangle = \begin{cases} |3/2,\ 3/2\rangle = |1,\ 1\rangle\alpha \\ |3/2,\ 1/2\rangle = (1/\sqrt{3})(|1,\ 1\rangle\beta + \sqrt{2}\,|1,\ 0\rangle\alpha) \\ |3/2,\ -1/2\rangle = (1/\sqrt{3})(|1,\ -1\rangle\alpha + \sqrt{2}\,|1,\ 0\rangle\beta) \\ |3/2,\ -3/2\rangle = |1,\ -1\rangle\beta \\ |1/2,\ 1/2\rangle = (1/\sqrt{3})(|1,\ 0\rangle\alpha - \sqrt{2}\,|1,\ 1\rangle\beta) \\ |1/2,\ -1/2\rangle = (1/\sqrt{3})(|1,\ 0\rangle\beta - \sqrt{2}\,|1,\ -1\rangle\alpha) \end{cases}$$

Momentum matrix element:
14 by 14 matrix (p, s*, p*)

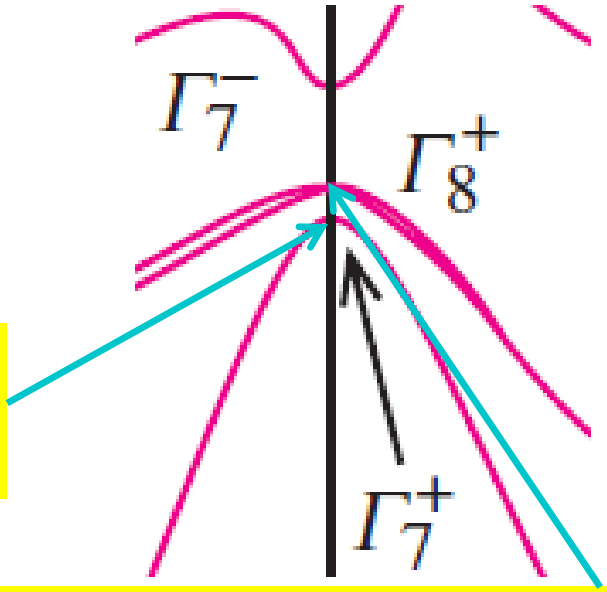
$$iQ = \langle X|p_y|\Gamma_{15c}(z)\rangle = \langle X|p_z|\Gamma_{15c}(x)\rangle$$

k·p theory: Application to valence bands at Γ

Momentum matrix elements:

$$iP = \langle X|p_x|\Gamma_1\rangle = \langle Y|p_Y|\Gamma_1\rangle = \langle Z|p_z|\Gamma_1\rangle$$

$$iQ = \langle X|p_y|\Gamma_{15c}(z)\rangle = \langle X|p_z|\Gamma_{15c}(x)\rangle$$



$$\frac{m_0}{m_{so}^*} = 1 - \frac{2}{3}\left[\frac{P^2}{m_0(E_0+\Delta_0)} + \frac{2Q^2}{m_0(E_0'+\Delta_0)}\right]$$

Inverse effective mass parameters A, B, C:

$$\frac{2m}{\hbar^2}A = 1 - \frac{2}{3}\left[\left(\frac{P^2}{mE_0}\right) + \left(\frac{2Q^2}{mE_0'}\right)\right]$$

$$\frac{2m}{\hbar^2}B = \frac{2}{3}\left[\left(\frac{-P^2}{mE_0}\right) + \left(\frac{Q^2}{mE_0'}\right)\right]$$

$$\left(\frac{2m}{\hbar^2}C\right)^2 = \frac{16P^2Q^2}{3mE_0mE_0'}.$$

$$m_{hh,lh}^{-1} = A \pm |B|\sqrt{1 + C^2/5B^2}$$

Also **Luttinger parameters**

$$\gamma_1 = -A, \quad \gamma_2 = -B/2,$$
$$\gamma_3 = \sqrt{(B^2/4) + (C^2/12)}$$

$$E_{\mathrm{lh,hh}} = -Ak^2 \pm \sqrt{B^2k^4 + C^2\left(k_x^2k_y^2 + k_y^2k_z^2 + k_z^2k_x^2\right)}$$

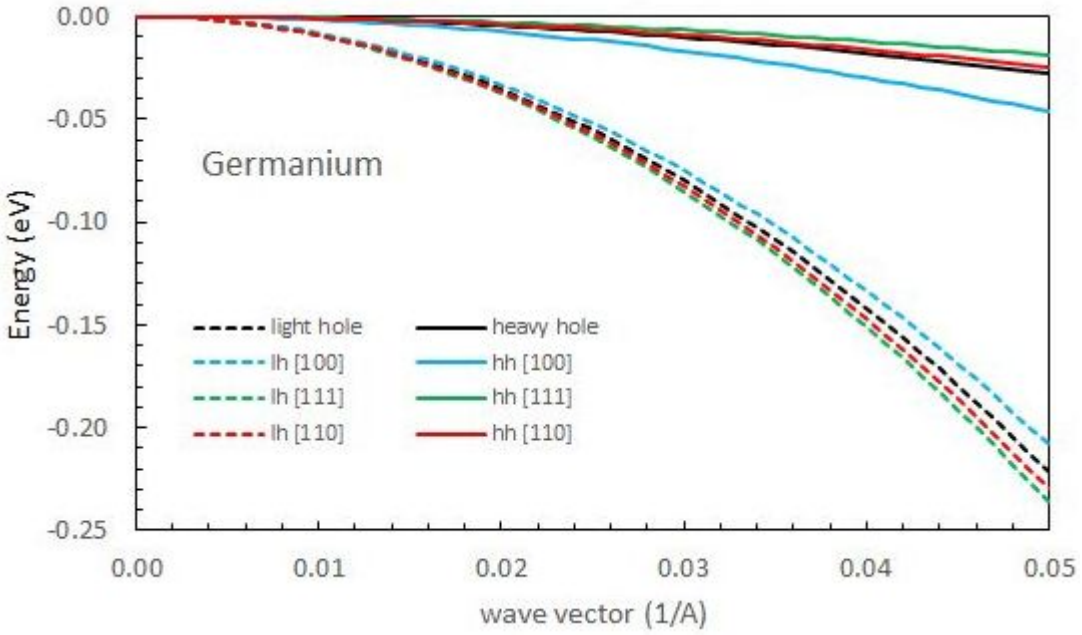
Yu & Cardona, Fundamentals of Semiconductors
Dresselhaus, Kip, Kittel, Phys. Rev. **98**, 368 (1955)

k·p theory: Application to valence bands at Γ

	A	B	$\lvert C \rvert^2$	Δ_0	m_{hh}/m_0		m_{lh}/m_0		m_{so}/m_0	
				[eV]	exp	th	exp	th	exp	th
C[b]	−2.5	0.2	4.6	0.013[a]		0.66[e]		0.29[e]		0.39[b]
Si[e]	−4.28	−0.68	24	0.044	0.54	0.50	0.15	0.15	0.23	0.24
Ge	−13.38	−8.5	173	0.295	0.34	0.43	0.043	0.041	0.095	0.1
SiC[c]	−2.8	−1.016	5.8	0.014		0.6		0.25		0.36
GaN[d]	−5.05	−1.2	34	0.017		0.5[e]		0.13[e]		0.2
GaP[e]	−4.05	−0.98	16	0.08	0.57	0.51	0.18	0.16		0.25
GaAs	−6.9	−4.4	43	0.341	0.53	0.73	0.08	0.08	0.15	0.17
GaSb	−13.3	−8.8	230	0.75	0.8	0.98	0.05	0.04		0.15
InP[e]	−5.15	−1.9	21	0.11	0.58	0.44	0.12	0.11	0.12	0.2
InAs	−20.4	−16.6	167	0.38	0.4	0.4	0.026	0.026	0.14	0.10
InSb	−36.41	−32.5	43	0.81	0.42	0.48	0.016	0.013		0.12
ZnS	−2.54	−1.5		0.07						
ZnSe	−2.75	−1.0	7.5	0.43		1.09		0.145		
ZnTe	−3.8	−1.44	14.0	0.93						
CdTe	−4.14	−2.18	30.3	0.92						

Yu & Cardona, Fundamentals of Semiconductors
Dresselhaus, Kip, Kittel, Phys. Rev. **98**, 368 (1955)

Valence Band Warping

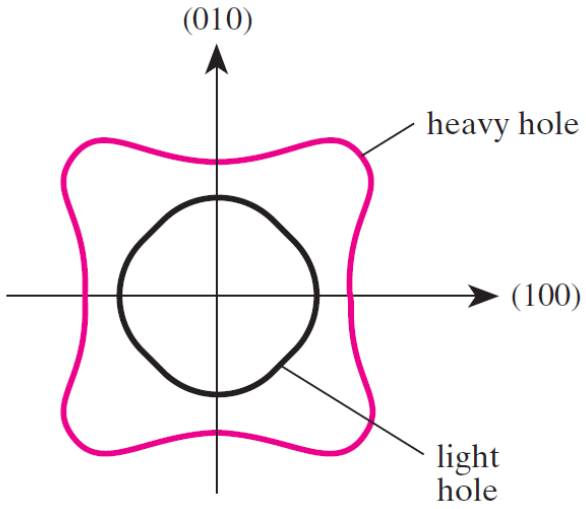


Hole effective mass depends on k-direction:

m_{hh} larger along (111)

m_{hh} smaller along (100)

Reversed for light hole.



Constant-energy surfaces

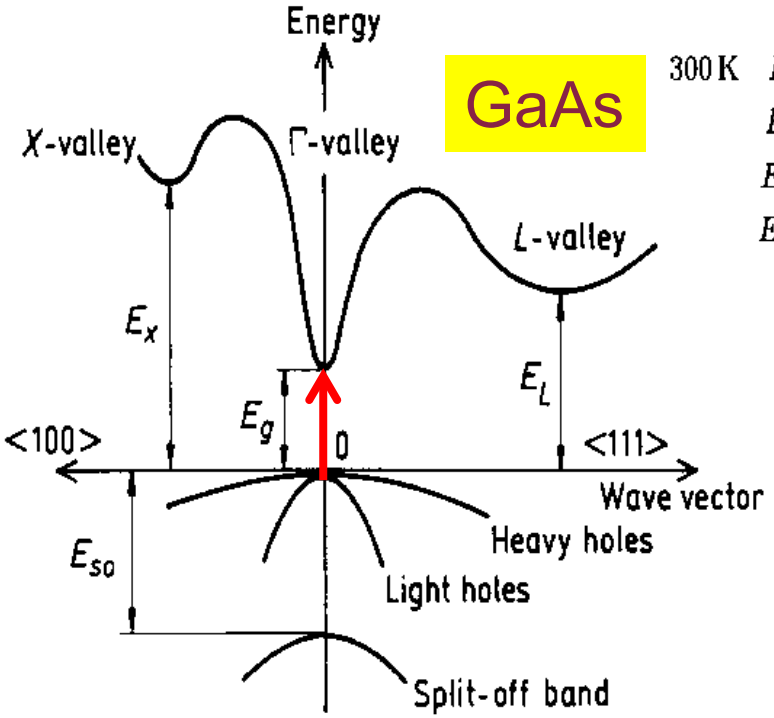
$$T = \sum_{i,j} \frac{\hbar^2 k_i k_j}{2 m_{ij} m_0}$$

$$(m_{ij})^{-1} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k_i \partial k_j}$$

Effective mass tensor

$$E_{\mathrm{lh,hh}} = -Ak^2 \pm \sqrt{B^2 k^4 + C^2\left(k_x^2 k_y^2 + k_y^2 k_z^2 + k_z^2 k_x^2\right)}$$

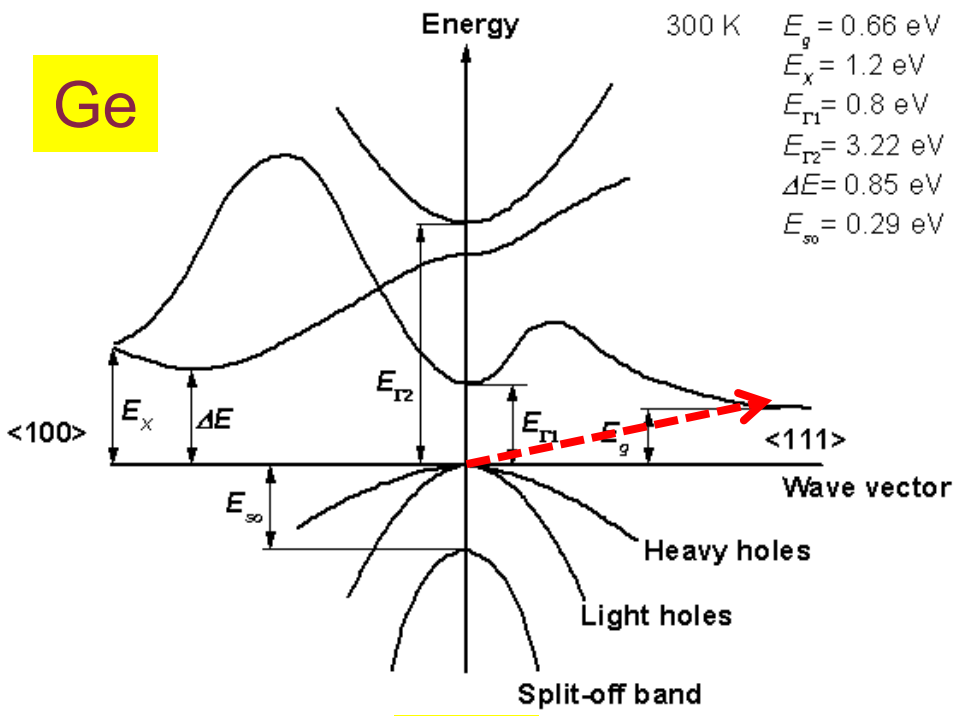
Semiconductor Band Structures



GaAs

300 K $E_g = 1.42$ eV
$E_L = 1.71$ eV
$E_X = 1.90$ eV
$E_{so} = 0.34$ eV

k=0



Ge

300 K $E_g = 0.66$ eV
$E_X = 1.2$ eV
$E_{Γ1} = 0.8$ eV
$E_{Γ2} = 3.22$ eV
$\Delta E = 0.85$ eV
$E_{so} = 0.29$ eV

k=0

Direct transition:

Initial and final electron state have **same** wave vector.

Indirect transition:

Initial and final electron state have **different** wave vector.

http://www.ioffe.ru/SVA/NSM/Semicond/index.html

Summary

- Band structure and Bloch's theorem
  - Examples: Si, Ge, Al, Cu, $SrTiO_3$

- Free-electron approximation
- Nearly free electron gas
- Empirical and ab initio pseudopotential methods

- **k.p** theory band structure method
- Effective masses, valence band warping, Luttinger parameters