Band Structure

Continued

Bloch theorem

Remarks on Blochfunctions

1. Quantum number k: <u>Crystal</u> momentum

$$\frac{\hbar}{i}\nabla\Psi_k = \frac{\hbar}{i}\nabla e^{i\,k\cdot r}u_k(\vec{r}) = \hbar k \cdot \Psi_k + \frac{\hbar}{i}e^{i\,k\cdot r}\nabla u_k(\vec{r})$$

2. k may be confined to the 1st BZ (Reduced BZ)

$$\Psi_{\vec{k}+\vec{G}} = e^{i\,\vec{k}\cdot\vec{r}}\,u_{\vec{k}+\vec{G}}(\vec{r})$$

3. Fourier expansion Bloch functions

   Periodicity $\quad \Psi(\vec{r}+p_i\cdot\vec{a}_i) = \Psi(\vec{r})$

$$u_k(\vec{r}) = \sum_{\vec{G}}C_{\vec{k}+\vec{G}}\cdot e^{i\,\vec{G}\cdot\vec{r}}$$

4. Band structure $\varepsilon_n(\vec{k})$

Band structure: Approaches

Last time

- Empty lattice (only periodicity)

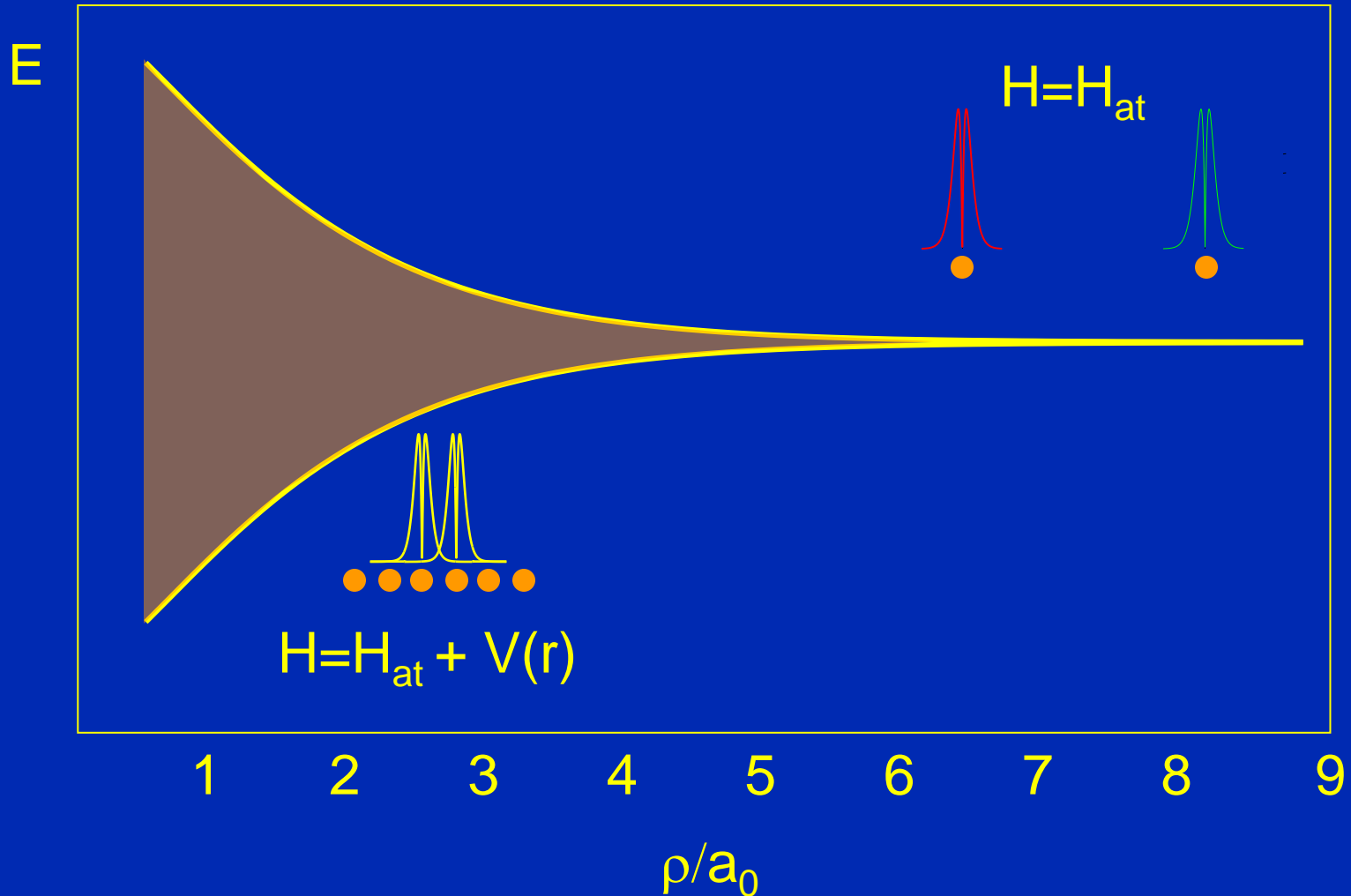- Perturbation theory (nearly free electrons, weak potential)

Today

- Tight binding method (LCAO)

Other methods

- Exact models (Kronig-Penney model, see book)

- 'advanced' methods: Ashcroft & Mermin chapter 11

Tight binding approach

E

$H=H_{at}$

$H=H_{at} + V(r)$

ρ/a_0

Tight binding

Atomic orbitals $\varphi(r)$: $H_{at}\,\varphi(r) = E_{at}\,\varphi(r)$

Solid state: $H = H_{at} + V(r)$

$$\Rightarrow \quad \Psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_j e^{i\,\vec{k}\cdot\vec{r}_j} \cdot \varphi(\vec{r} - \vec{r}_j)$$

1st order correction to energy: diagonal elements

$$\langle k|H|k \rangle = \frac{1}{N} \sum_j \sum_m e^{i\,\vec{k}\cdot(\vec{r}_j - \vec{r}_m)} \cdot \langle \varphi_m|H|\varphi_j \rangle$$

$$= \sum_m e^{i\,\vec{k}\cdot\vec{\rho}_m} \cdot \int dV\, \varphi^*(\vec{r} - \vec{\rho}_m) H \varphi(\vec{r})$$

Tight binding

$$\langle k | H | k \rangle = \sum_m e^{i\vec{k}\cdot\vec{\rho}_m} \cdot \int dV \; \varphi^*(\vec{r} - \vec{\rho}_m) H \varphi(\vec{r})$$

Only nearest neighbours:

Self $\qquad \rho = 0 \quad \Rightarrow \quad \int dV \; \varphi^*(\vec{r}) H \varphi(\vec{r}) \equiv -\alpha$

N.N. $\quad \rho_m = \rho \quad \Rightarrow \quad \int dV \; \varphi^*(\vec{r} - \vec{\rho}) H \varphi(\vec{r}) \equiv -\gamma$

$$\varepsilon(k) = \langle k | H | k \rangle = -\alpha - \gamma \cdot \sum_{nn} e^{-i\vec{k}\cdot\vec{\rho}_{nn}}$$

Tight binding

$$\varepsilon(k) = \langle k | H | k \rangle = -\alpha - \gamma \cdot \sum_{nn} e^{-i\,\vec{k}\cdot\vec{\rho}_{nn}}$$

S.C.: n.n. at (±a, 0, 0); (0, ±a, 0); (0, 0, ±a)

$$\varepsilon(k) = -\alpha - 2\gamma \left[\cos(k_x a) + \cos(k_y a) + \cos(k_z a) \right]$$
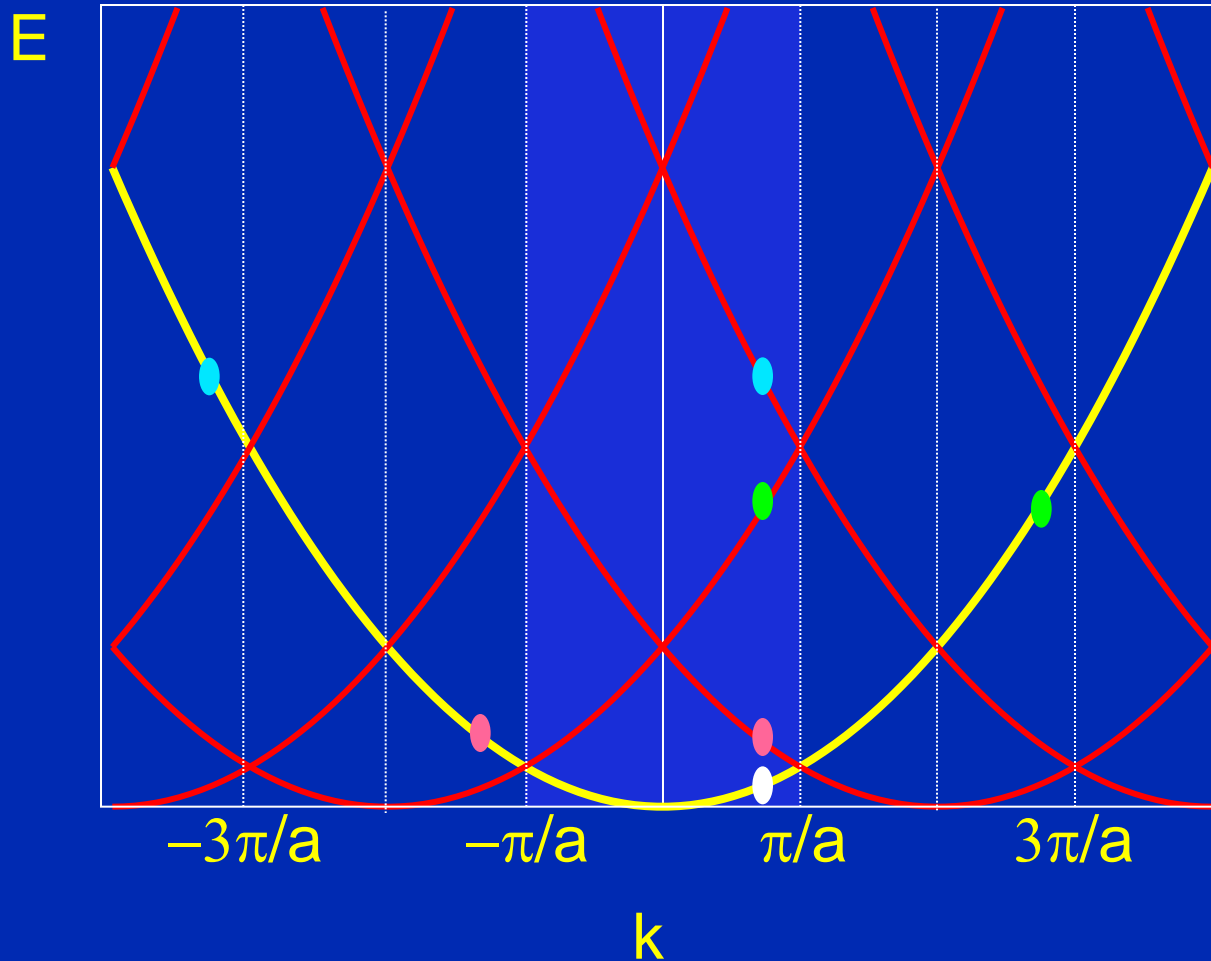
E $-\alpha$ ┤

4γ in the (100) dir.

$(k_x, 0, 0)$
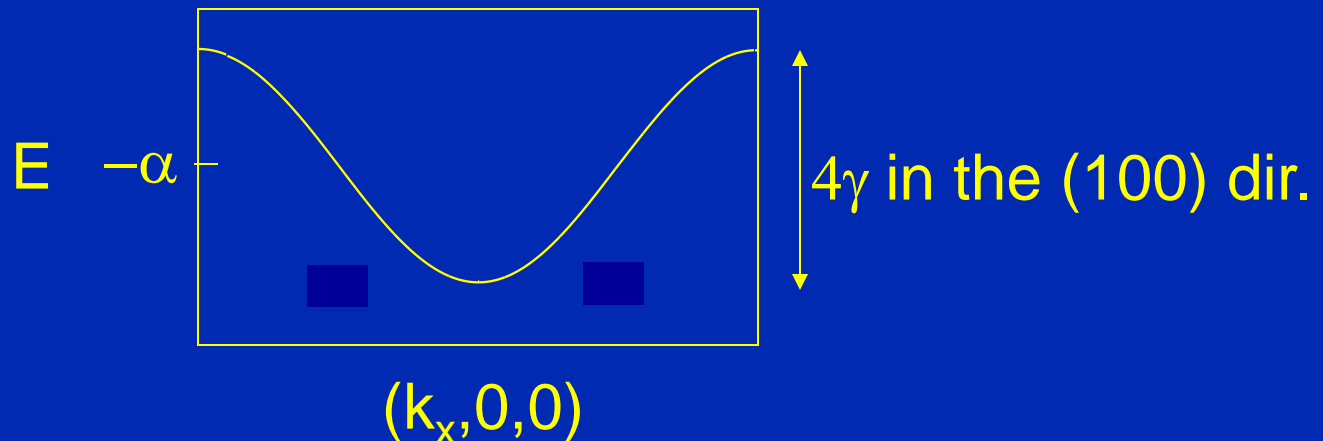
Tight binding

- TB method: Insulators and core electrons and d-electrons in transition metals (e.g. Cu, V, Ti etc.).
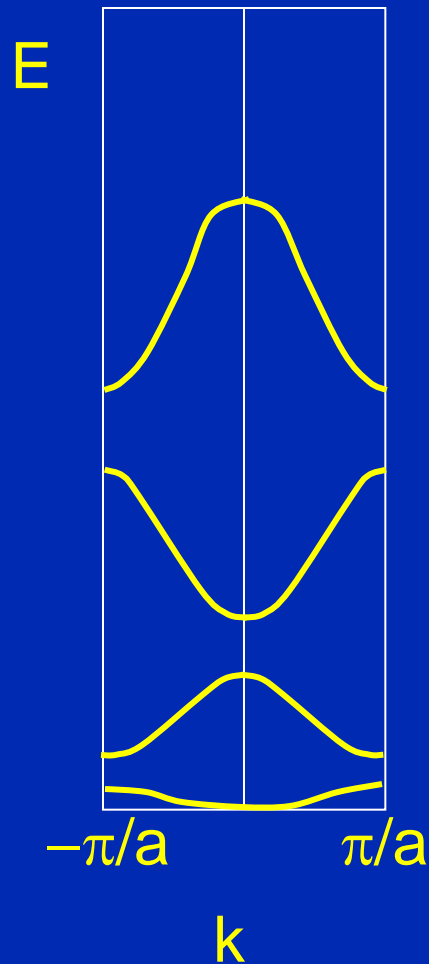- Nearly free electron model: conduction electrons, s or p, alkali (e.g. Na, K, etc.)

Reduced Brillouin zone
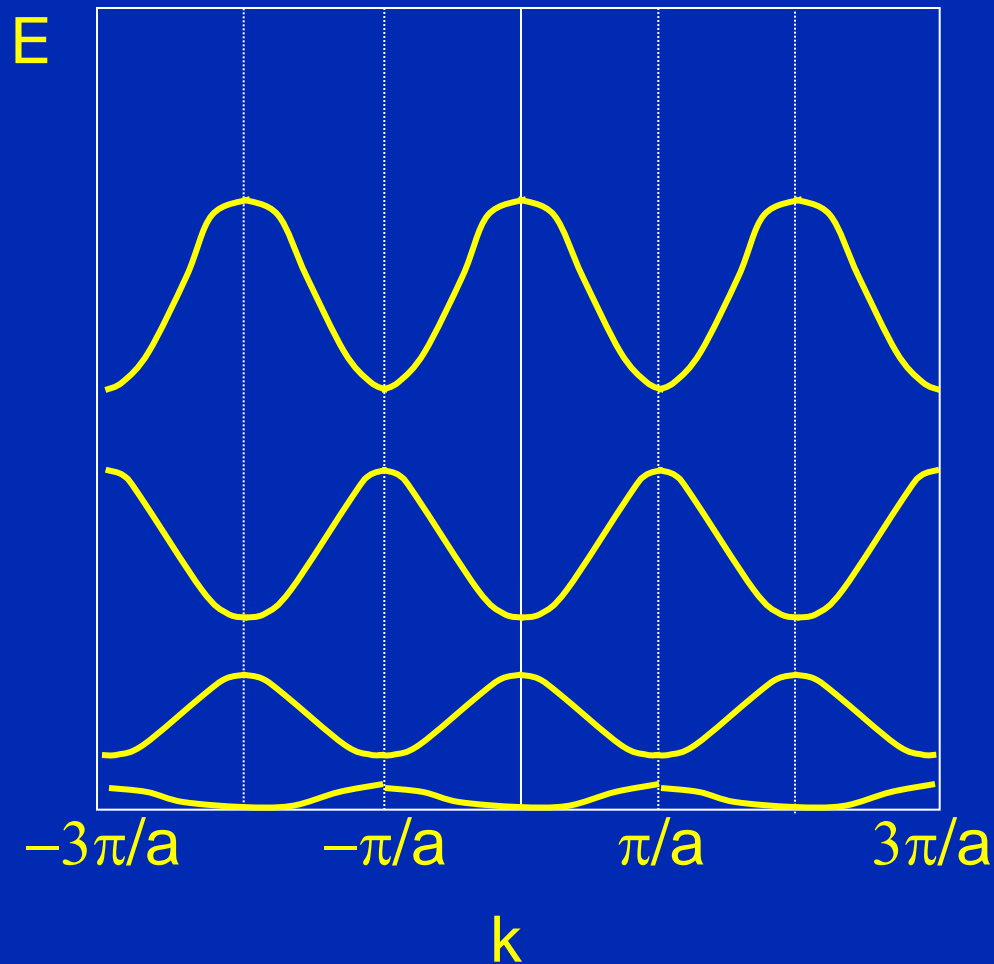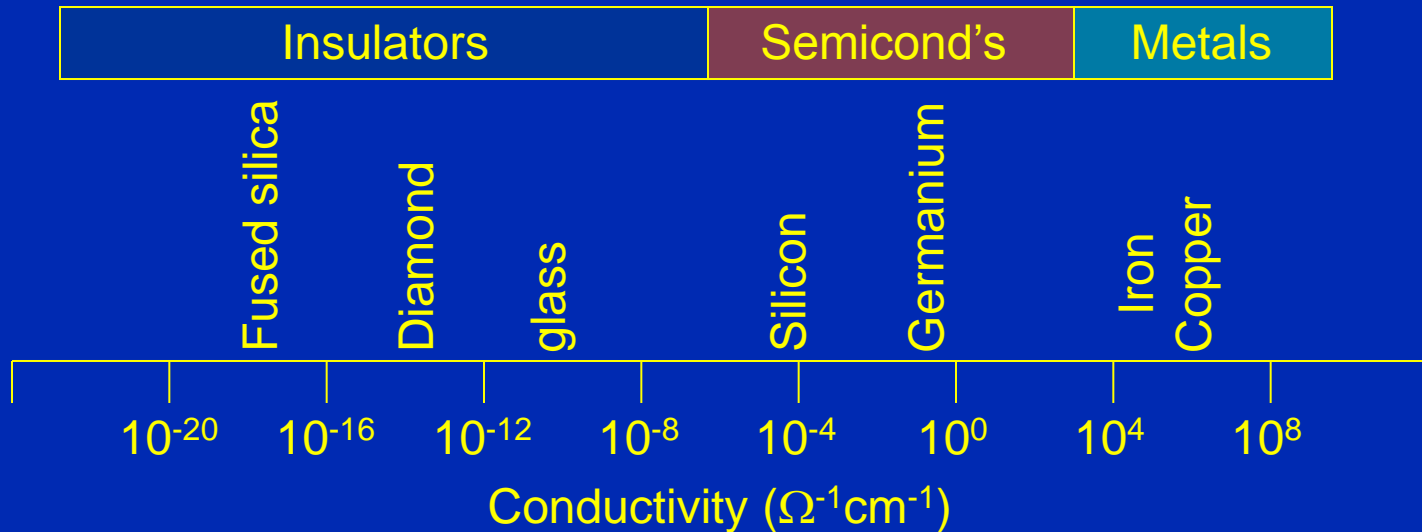
Extended zone scheme
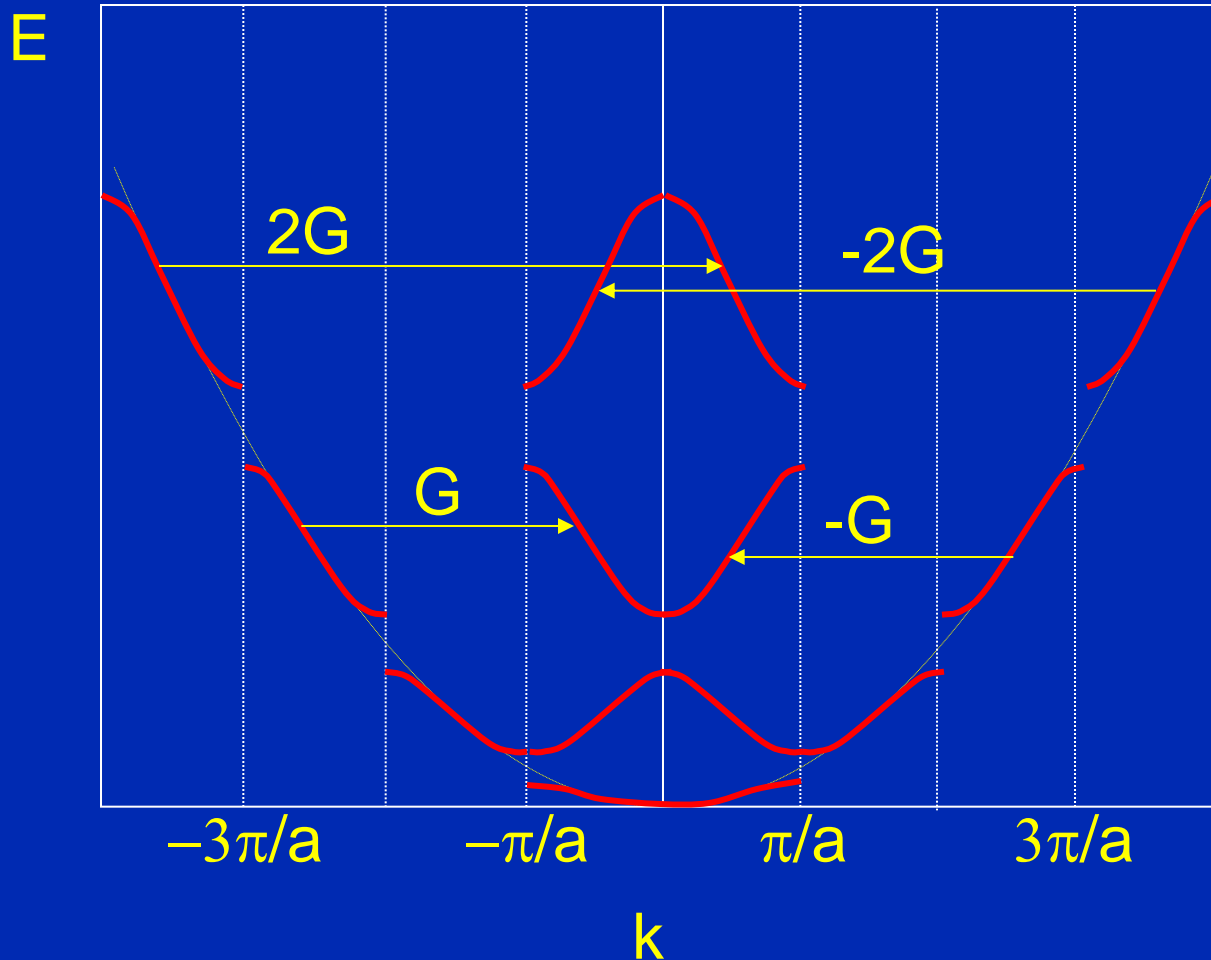
Reduced zone scheme

Periodic zone scheme

$$E_{n,\vec{k}+\vec{G}} \equiv E_{n,\vec{k}}$$
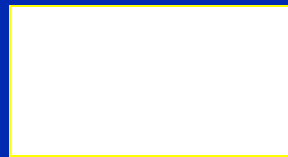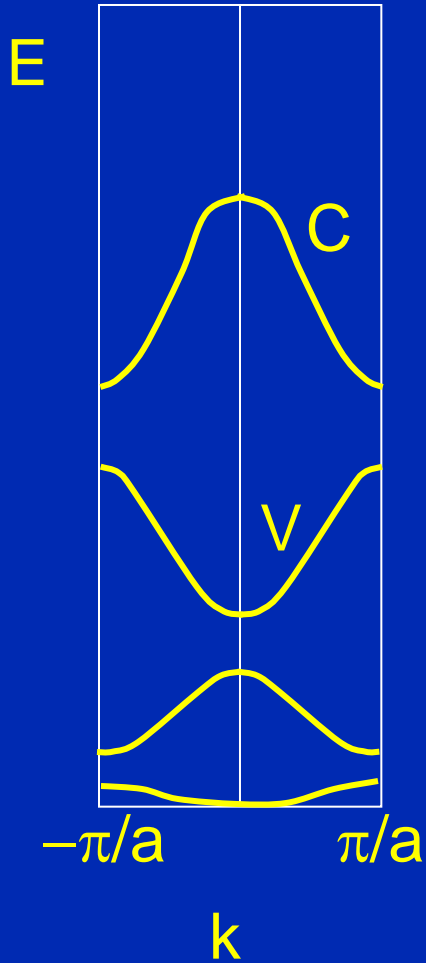
Bandstructure

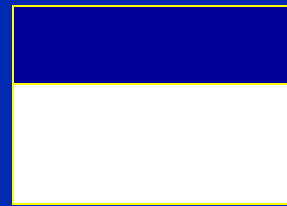- Why are not all solids metals

- Why is diamond an insulator
- Why is copper a metal
- Why does the conductivity of Si increase upon heating

Conductivity

$$\sigma = n \cdot e \cdot \mu$$

| Insulator | Metal | p-Doped Semi-Conductor | n-Doped Semi-Conductor |

Diamond and Germanium
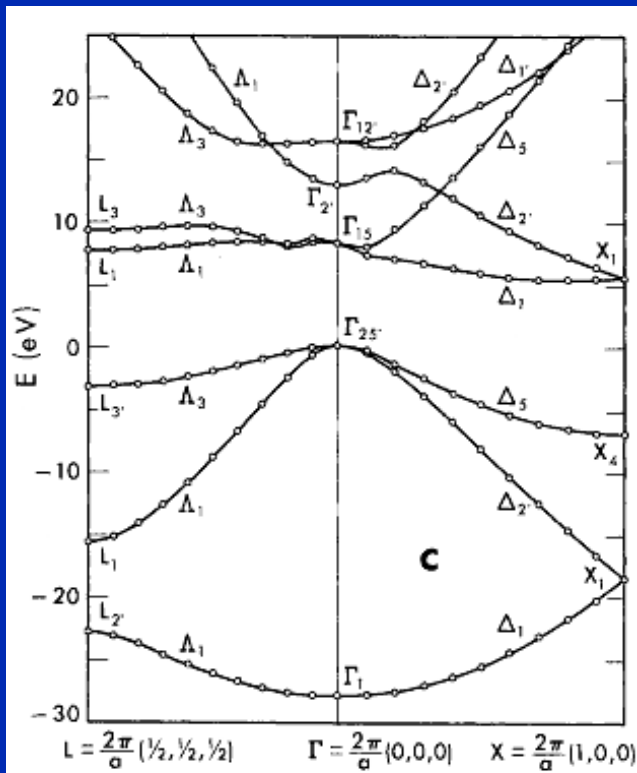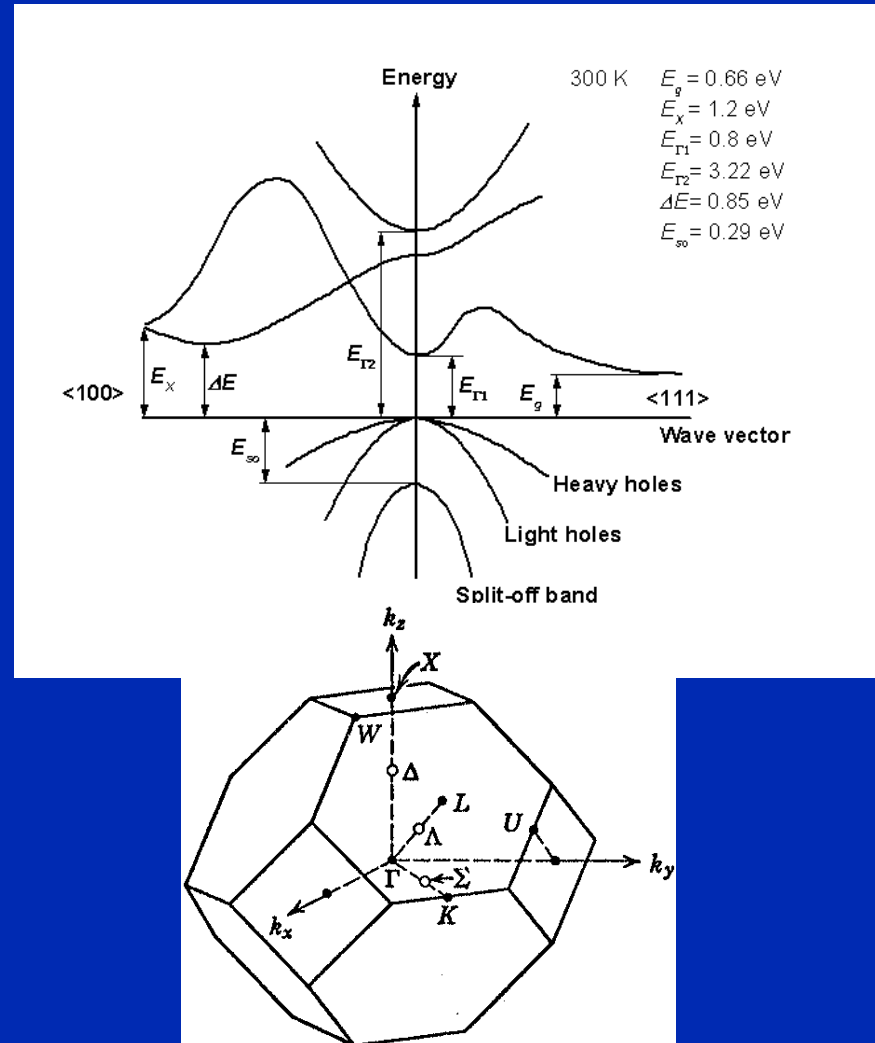
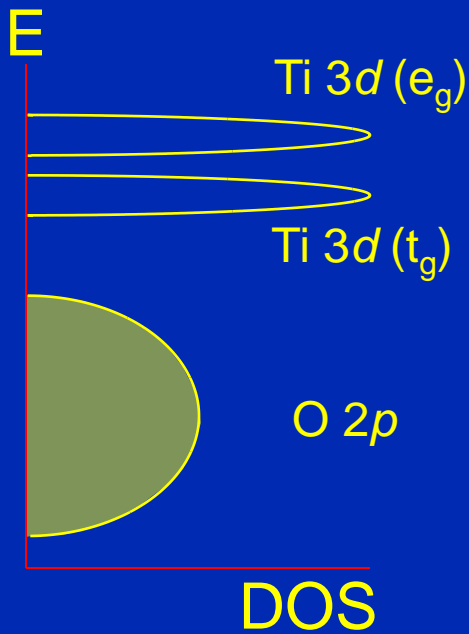## Germanium (E_g=0.7 eV)

Diamond (E_g=5.5 eV)

FIG. 1. The electronic band structure of diamond.
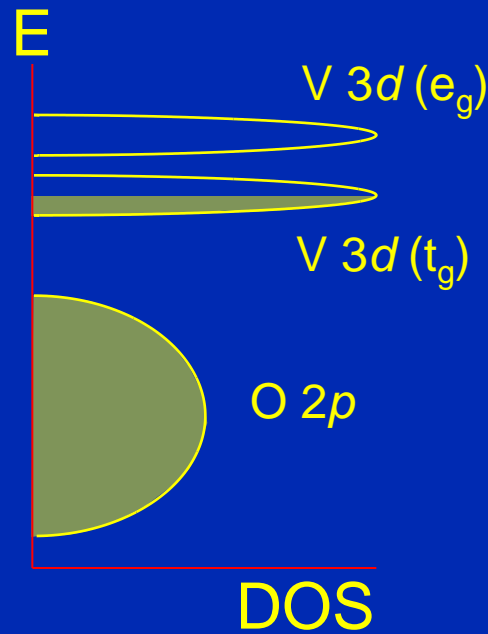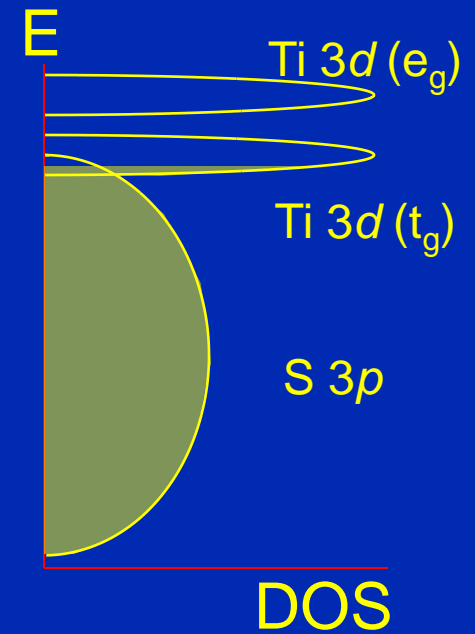
Bandfilling & overlap

E

Ti 3d (e$_g$)

Ti 3d (t$_g$)

O 2p

DOS

E

V 3d (e$_g$)

V 3d (t$_g$)

O 2p

DOS

E

Ti 3d (e$_g$)

Ti 3d (t$_g$)

S 3p

DOS

TiO_2
Empty d-bands

VO_2
Partially filled d-bands

TiS_2
Overlapping bands

Ti: [Ar]3$d^2$4s^2
V: [Ar]3$d^3$4s^2

Band gap in some materials

		E_g(eV)
Diamond	I	5.4
Si	I	1.17
Ge	I	0.74
GaAs	d	1.52
GaSb	d	0.81
Te	d	0.33
ZnO		3.44
Cu_2O	d	2.17
CdTe	d	1.6
TiO_2		3.03

Conduction

Forbidden E_g

Valence
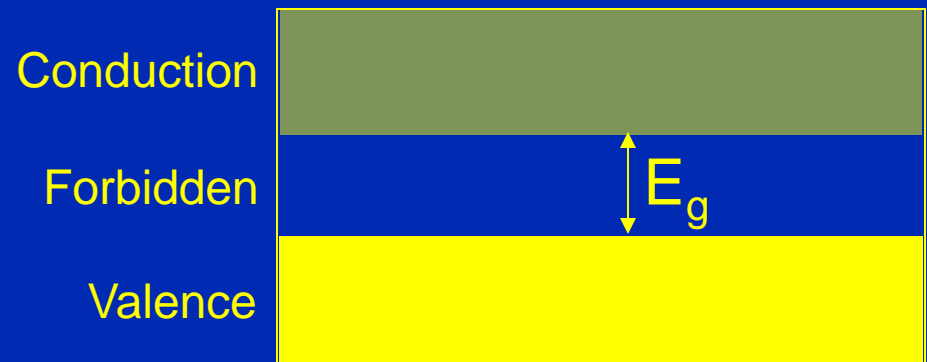
→ Direct & indirect
Optical absorption

GaAs

Si