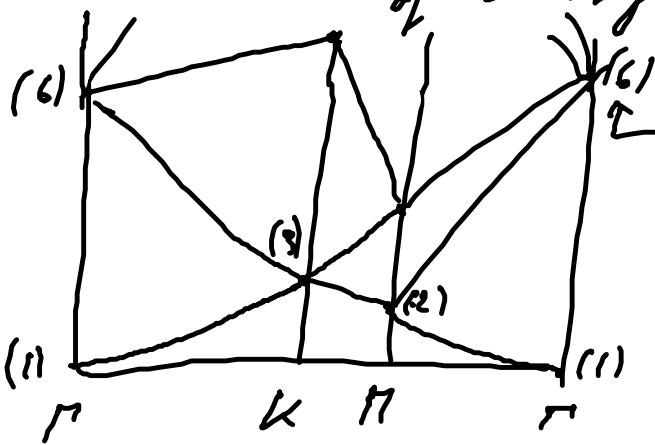


of hexagonal lattice
the irreducible part of the BZ
if we know $E_n(\vec{k})$, $\psi(\vec{k}, \vec{r})$ in this
region, we know them everywhere.

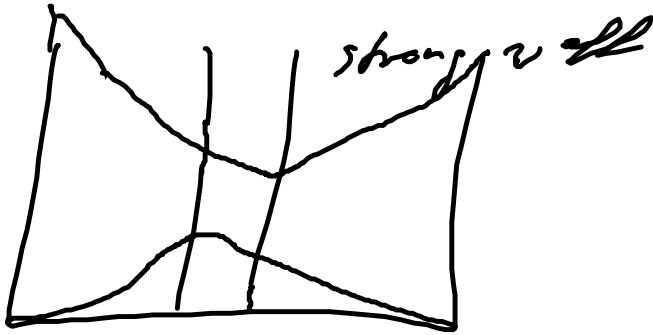
$v_{eff} = 0$ = jellium, but the translational symmetry of a crystal \Rightarrow free electron band structure



degeneracy of band (without spin degeneracy)

\equiv free electron parabola folded back to the

How does this change when $v_{eff} \neq 0$



from $\frac{1}{\sqrt{V_g}} e^{i(\vec{k} + \vec{G}) \cdot \vec{r}}$ = free electron
to $\psi_n(\vec{k}, \vec{r}) = \sum_{\vec{G}_n} c_{\vec{G}_n}(\vec{k}) e^{i(\vec{k} + \vec{G}_n) \cdot \vec{r}}$

eigenvalue change

from $\frac{\hbar^2}{2m} (\vec{k} + \vec{G}_n)^2$

to $E_n(\vec{k}) = \frac{\hbar^2}{2m} (\vec{k} + \vec{G}_n)^2 + \Delta_n(\vec{k})$

For non-generated states the change is small $\sim |v_{eff} / \epsilon_n|^2$

If it large for degenerate states: $\sim 1/v_{\text{cell}}(E_n)$
What can we learn from a bandstructure?

- nature of bonding
- chemically active states
- optical excitations (photoemission)
- transport properties (metal/semiconductor/insulator)

N -electron: N lowest-energy states are occupied
 each state $|n, \vec{k}\rangle$ can be filled with 2 electrons: ↑ and ↓

One band $E_n(\vec{k})$, fixed n , $\vec{k} \in \text{BZ}$,

can be occupied by $2 \int_{\text{BZ}} \frac{V_g}{(2\pi)^3} d^3\vec{k}$ electrons

$$= 2 \frac{V_g}{(2\pi)^3} \frac{(2\pi)^3}{\Omega} = 2 \frac{V_g}{\Omega} = \dots = 2 \hat{N}$$

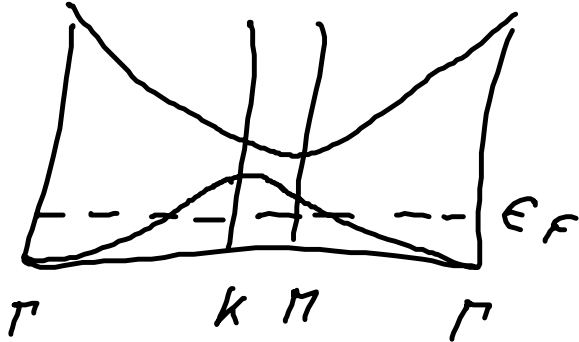
\uparrow system density of \vec{k} points
 \uparrow volume of prim. unit cell

\hat{N} = number of prim. unit cells in the
 base volume V_g .

One band can be filled with up to 2
 electrons per primitive unit.

3 EXAMPLES

Material 1: Material built from atoms such that we have 1 electron per prim. cell
 (Li, Na, Cu, Ag, Au) one valence electron

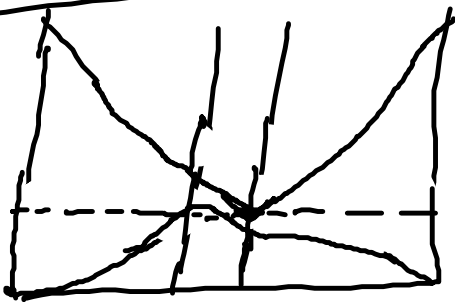


Fermi level cuts the band in the middle

\Rightarrow immediately above highest occupied states there are empty states.

The lowest energy to excite an electron is infinitesimally small. Such systems are called metals, conductors.

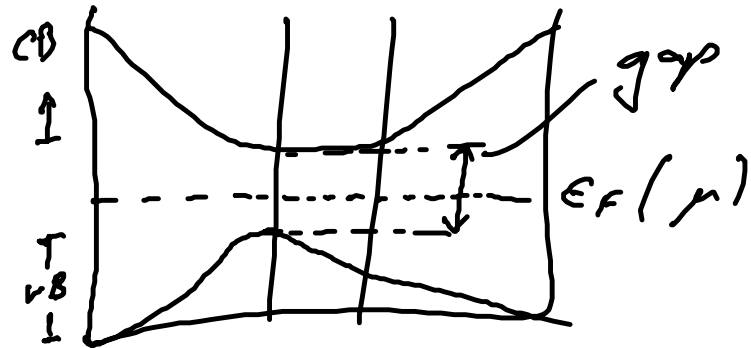
Material 2: 2 electrons per prim. cell & weak v_{eff}



The second band gets partially occupied before the first band is completely full.

E_F cuts through bands \Rightarrow conductor

Material 3 2 electrons per cell, band structure of "strong v_{eff}"



The Fermi energy E_F in the bandgap

The fully occupied band is called valence band (VB)
 at $T=0K$

The band above it is called conduction band (CB)

The size of the gap determines the appearance of the material.

$$E_{gap} = I - A = E^{N-1} + E^{N+1} - 2E^N$$

$$\approx E_{CB}^{N-\frac{1}{2}} - E_{VB}^{N+\frac{1}{2}} \leftarrow \text{in the transition state concept}$$

$$= E_{CB}^N - E_{VB}^N + \Delta^{xc}$$

Note on $E_{gap} \approx$ Friedg on Tuesday:

(many body perturbation theory, electron self energy) \equiv Compton theory & experiment shows that LDA (and GGA) results for the Kohn-Shan band gap ($E_{CB}^N - E_{VB}^N$) differ from exp data by $\approx 50\%$.

If $E_{gap} < \text{tw-visible light}$
 the material looks like a metal, e.g. Si: $E_{gap} = 1.1eV$

GeAs: $E_{gap} = 1.45eV$ // visible light
 $1.65eV < \text{tw} < 3.1eV$

If E_{gap}

If E_{gap} is in the range of visible light
the material is transparent

e.g. GaP $E_{gap} = 2.3 \text{ eV}$

\Rightarrow looks orange

diamond $E_{gap} \approx 6 \text{ eV}$ \approx fully transparent.

semiconductor typical definition: $E_{gap} \approx k_B T$

$$k_B \cdot T = 0.026 \text{ eV at room temp.}$$

\Rightarrow semiconductor has band gap $\approx 3-4 \text{ eV}$

In view; More relevant: A semiconductor

is an insulator that can be doped, i.e.

impurity atoms can be added to create

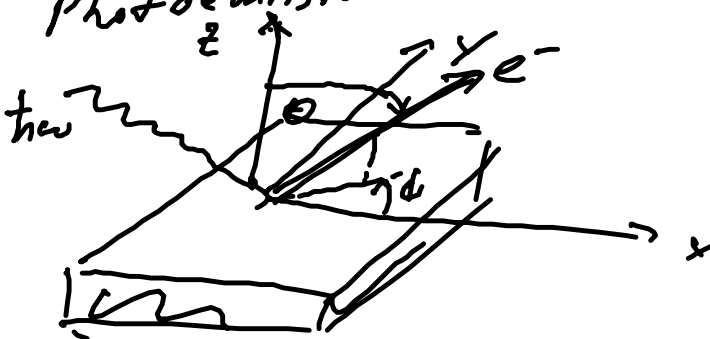
electrons in the CB or holes in the VB.

With definition as diamond

is a semiconductor

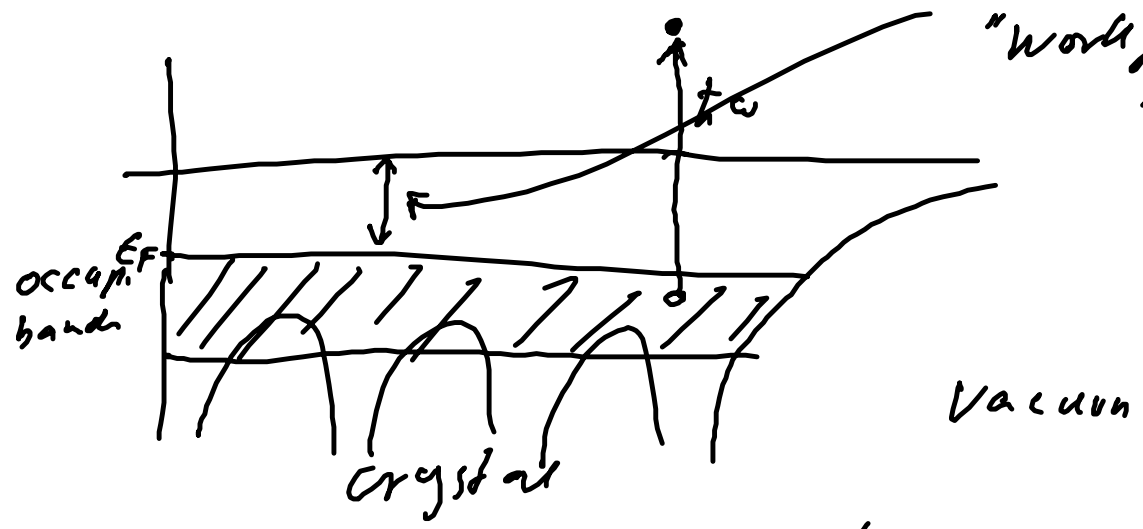
What is calculated and what is measured?

Photoemission & inverse photoemission



measured is intensity
 $I(h\nu, \theta, \phi, E)$

energy between E_F and vacuum level:
"work function"
 $\approx 4 - 5 eV$



GaAs example empirical (pseudo) potential
not DFT.

DFT: the agreement is nearly as
good for the bands. But not for

the gap.

inverse photoemission

shoot in electrons; they loose energy and emit light \Rightarrow information about empty states.

General properties of $E_n(\vec{k})$

continuity of $E_n(\vec{k})$ and the physics of the first and second derivative of $E_n(\vec{k})$.

$$\hbar \nabla_{\vec{k}} \psi_{n\vec{k}}(\vec{r}) = \left(\frac{-\hbar^2}{2m} + v_{eff} \right) \psi_{n\vec{k}}(\vec{r})$$

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

$$\hbar \nabla_{\vec{k}} \psi_{n\vec{k}} = e^{i\vec{k}\vec{r}} \left(\frac{-\hbar^2}{2m} \nabla^2 + v_{eff} + \frac{\hbar^2}{2m} k^2 - 2 \frac{\hbar^2}{2m} i\vec{k}\vec{r} \right) u_{n\vec{k}}(\vec{r})$$
$$= E_n(\vec{k}) \cdot e^{i\vec{k}\vec{r}} u_{n\vec{k}}(\vec{r})$$

$$E_n(\vec{k}) = \int u_{n\vec{k}}^*(\vec{r}) \tilde{H} u_{n\vec{k}}(\vec{r}) d^3\vec{r}$$

$$\text{with } \tilde{H} = \frac{-\hbar^2}{2m} \nabla^2 + v_{eff}(\vec{r}) + \frac{\hbar^2}{2m} k^2 - 2 \frac{\hbar^2}{2m} i\vec{k}\vec{r}$$

\uparrow we only need to consider one unit cell and periodic eigenfunctions.

$$\tilde{H} u_{n,\vec{k}}(\vec{r}) = E_{n,\vec{k}} u_{n,\vec{k}}(\vec{r})$$

look at neighborhood of $E_n(\vec{k})$

$$E_n(\vec{k} + \vec{x}) = \int U_{n, \vec{k} + \vec{x}}(\vec{r}) \tilde{h}(\vec{k} + \vec{x}) U_{n, \vec{k} + \vec{x}}(\vec{r}) d^3r$$

$$\tilde{h}(\vec{k} + \vec{x}) - \tilde{h}(\vec{k}) = \frac{\hbar^2}{2m} (\vec{x}^2 + 2\vec{k} \cdot \vec{x}) - \frac{\hbar^2}{2m} 2i\vec{x} \cdot \vec{\nabla}$$

shows for small x also $\tilde{h}(\vec{k} + \vec{x}) - \tilde{h}(\vec{k})$ is small.

use perturbation theory

$$E_n(\vec{k} + \vec{x}) = \int U_{n, \vec{k}}^*(\vec{r}) \tilde{h}(\vec{k}) U_{n, \vec{k}}(\vec{r}) d^3r \quad \text{0. order part. theory}$$

$$+ \int U_{n, \vec{k}}^*(\vec{r}) \left[\frac{\hbar^2}{2m} (\vec{x}^2 + 2\vec{k} \cdot \vec{x}) - \frac{\hbar^2}{2m} 2i\vec{x} \cdot \vec{\nabla} \right] U_{n, \vec{k}}(\vec{r}) d^3r \quad \text{1. order part. theory}$$

$$+ \sum_{l \neq n} \frac{\left| \int U_{n, \vec{k}}(\vec{r}) \left[\frac{\hbar^2}{2m} (\vec{x}^2 + 2\vec{k} \cdot \vec{x}) - \frac{\hbar^2}{2m} 2i\vec{x} \cdot \vec{\nabla} \right] U_{l, \vec{k}}(\vec{r}) d^3r \right|^2}{E_n(\vec{k}) - E_l(\vec{k})} \quad \text{2. order part. theory}$$

$$+ O(x^3)$$

momentum operator: $\vec{p}_{n, m} = \langle \psi_{n, \vec{k}} | \frac{\hbar}{i} \vec{\nabla} | \psi_{m, \vec{k}} \rangle$

$$\stackrel{\text{Block}}{\text{+ Leon}} \langle U_{n, \vec{k}} | \hbar \vec{k} + \frac{\hbar}{i} \nabla | U_{m, \vec{k}} \rangle$$

$$E_n(\vec{k} + \vec{x}) - E_n(\vec{k}) = \frac{\hbar}{m} \vec{x} \cdot \vec{p}_{nn} + \frac{\hbar^2}{2m} x^2$$

$$+ \frac{\hbar^2}{2m} \sum_{l \neq n} \frac{|\vec{x} \cdot \vec{p}_{n, l}|^2}{E_n(\vec{k}) - E_l(\vec{k})} + O(x^3)$$

$\Rightarrow E_n(\vec{k})$ is continuous in \vec{k}

$$\vec{\nabla}_{\vec{k}} E_n(\vec{k}) = \frac{\hbar}{m} \vec{p}_{nn}$$

or

$$\vec{p}_{nn} = \frac{m}{\hbar} \vec{\nabla}_{\vec{k}} E_n(\vec{k})$$

The expectation value of the momentum operator is no longer $\sim \hbar \vec{k}$ — as it was for electrons — but given by $\vec{\nabla}_{\vec{k}} E_n(\vec{k})$.