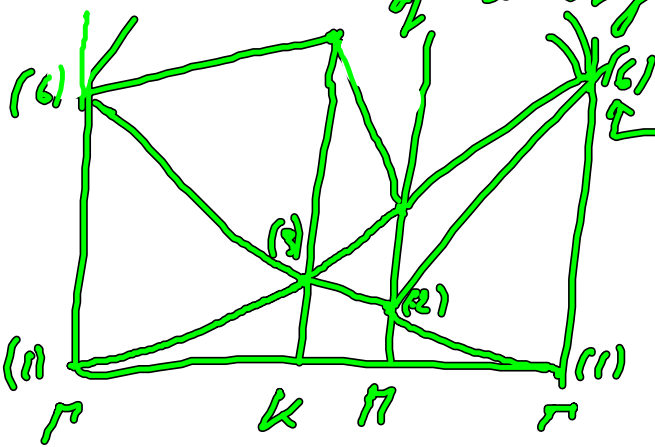


of hexagonal lattice
 the irreducible part of the BZ
 if we know $\epsilon_n(\vec{k})$, $\psi_n(\vec{k}, \vec{r})$ in this
 region, we know them everywhere.

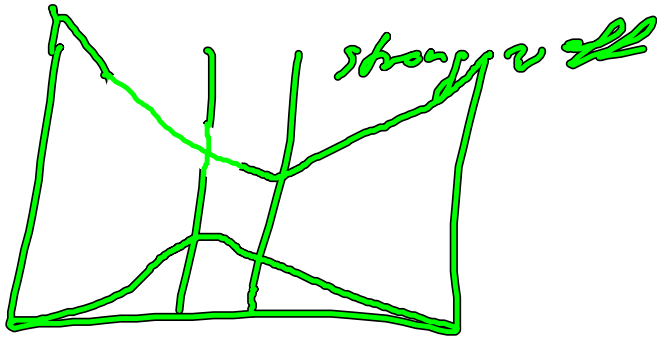
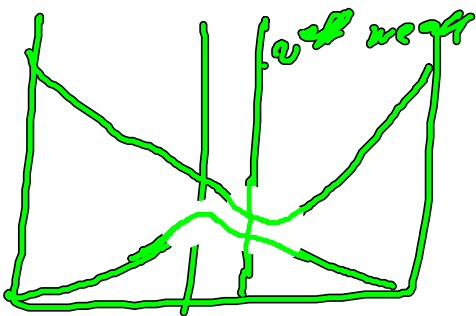
$v_{eff} = 0$ = jellium, but the translational symmetry of a crystal \Rightarrow free electron band structure



degeneracy of band (without spin degeneracy)

= free electron parabol. 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 $\varphi_n(\vec{k}, \vec{r}) = \sum_{\vec{G}_n} c_{\vec{G}_n}(\vec{k}) e^{i(\vec{k} + \vec{G}_n) \cdot \vec{r}}$

eigenvalue change

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

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

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

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

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

N -electrons: 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

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

↑ volume of prim. unit cell

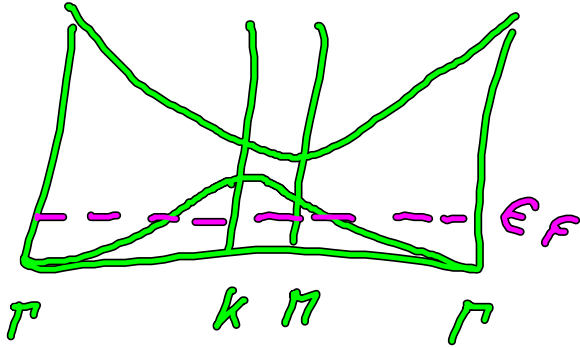
↑ spin density of \vec{k} points

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

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

3 EXAMPLES

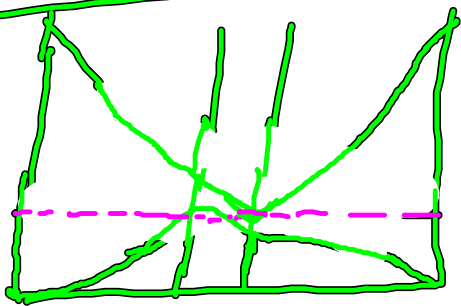
Material 1: Material built from atoms such that we have 1 electron per prim. cell (Li, Na, Cu, Ag, Au) ^{on} valence electron



Fermi level cuts the band in the middle

⇒ 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.

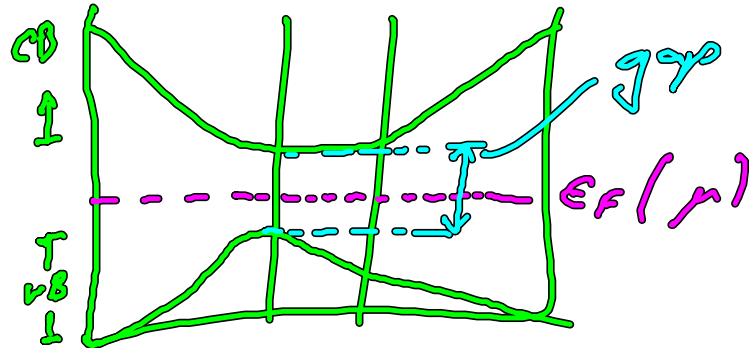
Material 2: 2 electrons per prim. cell & weak v_{th}



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

E_F cuts through bands ⇒ conductor

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



The Fermi energy lies in the band gap

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 $E_{gap} \approx$ Friday or Tuesday:

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

If $E_{gap} < \text{to-visible light}$
 the material looks like a metal, e.g. Si: $E_{gap} = 1.1eV$
 GaAs: $E_{gap} = 1.45 eV$ // visible light $1.65 eV < \text{to} < 3.1 eV$
 If E_{gap}

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

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

\Rightarrow looks orange

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

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

$k_B \cdot T = 0.025 \text{ eV}$ at room temp.

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

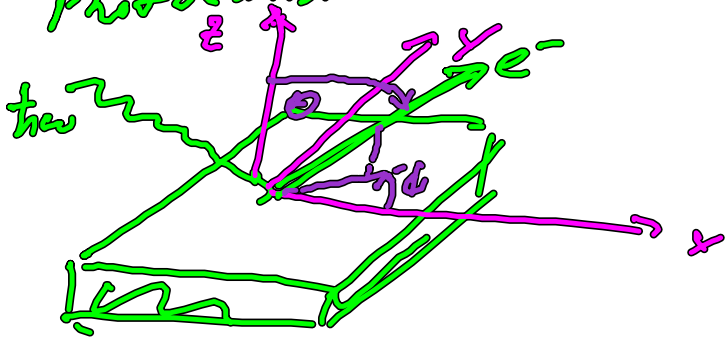
in view: More relevant: A semiconductor
is an insulator that can be doped, i.e.
impurity atoms can be added to create
electrons in the CB or holes in the VB.

with definition as diamond

is a semi-conductor

What is calculated and what is measured?

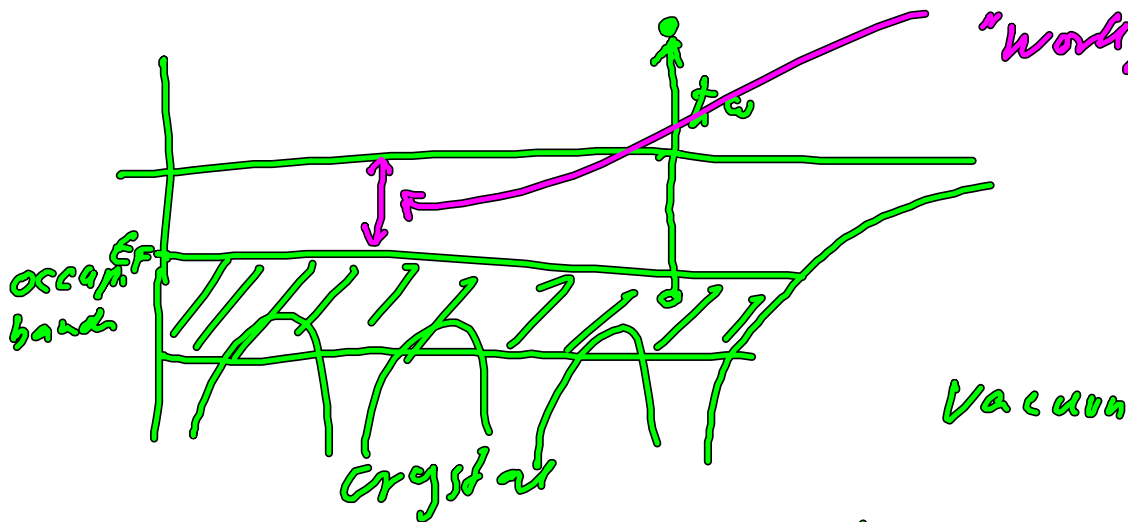
Photoemission & reverse photoemission



measured is
intensity

$$I(h\nu, \theta, \phi, \epsilon)$$

energy between E_F
and vacuum level:
"work function"
 $\approx 4.5 \text{ eV}$



G. A: example empirical (pseudo) potential
not DFT.

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

fb sep.

inverse photoemission

shoot in electrons; they loose energy and emit light \Rightarrow information about crystal state.

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

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

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

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

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

$\uparrow \nabla^2$

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

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

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

\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 neighbor behavior of $E_n(\vec{k})$

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

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

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

use perturbation theory

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

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

$$+ \sum_{l \neq n} \frac{\left| \int u_{n, \vec{k}}(\vec{r}) \left[\frac{\hbar^2}{2m} (\vec{x}^2 + 2\vec{k}\vec{x}) - \frac{\hbar^2}{2m} 2i\vec{x}\vec{\nabla} \right] u_{l, \vec{k}}(\vec{r}) d^3r \right|^2}{E_n(\vec{k}) - E_l(\vec{k})} \quad \text{1. order pert. theory}$$

$$+ O(x^3)$$

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

$$\stackrel{\text{Block}}{\sim} \langle u_{n, \vec{k}} | \frac{\hbar}{i} \vec{\nabla} + \frac{\hbar}{i} \vec{\nabla} | u_{n, \vec{k}} \rangle$$

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

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

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

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

or

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

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