

XIII. Topics in Semiconductor Physics

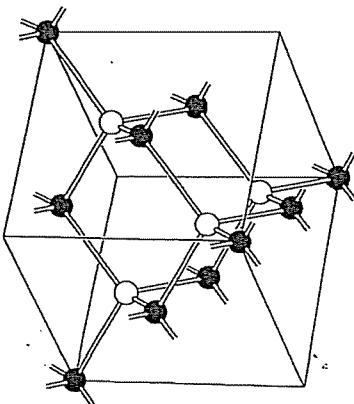
XIII-①

A. Materials

	Si	E_g (room temp.)
Group IV	Ge α Si	1.1eV 0.7eV 0.08eV
III-V	GaAs GaP GaAs InAs InP	1.4eV 2.3eV 0.7eV 1.3eV 2.6eV
II-VI	CdS CdTe ZnS ZnTe PbS PbTe	1.5eV 3.6eV 2.3eV 0.4eV 0.3eV

B. Crystal Structure

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• FCC

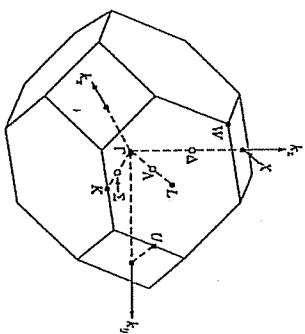
• Each lattice point is decorated by two atoms

• Si, Ge:

two identical atoms
(diamond structure)

- GaAs, etc.:
 - 1 Ga, 1 As for each lattice point (zinc-blende structure)
 - Each atom has 4 nearest neighbors forming a tetrahedral (sp^3 hybridization), covalent bonds
 - reciprocal lattice is a bee

1st O.Z.



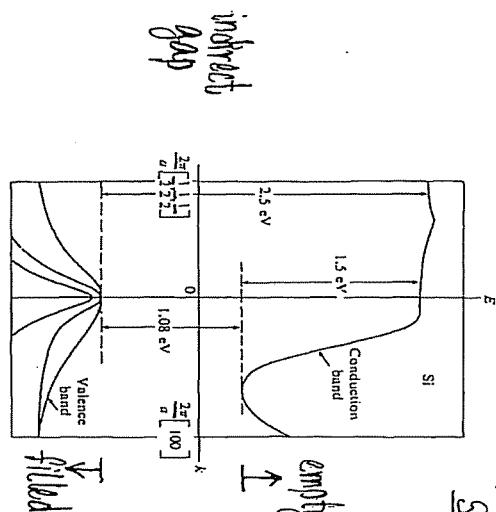
C. Some band structure

III-③

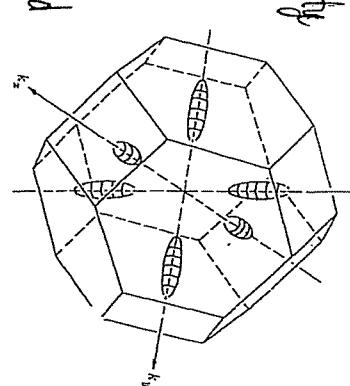
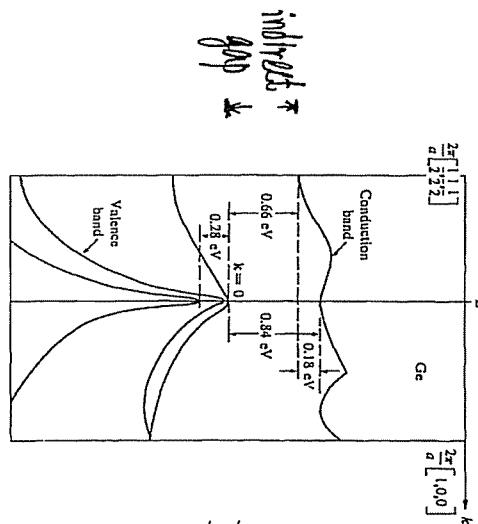
Graph

III-④

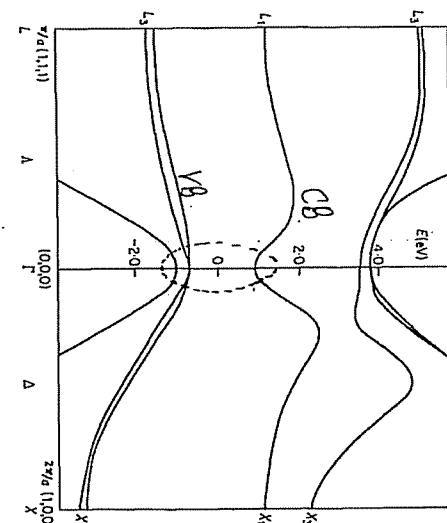
Silicon
1st B.Z. showing
constant energy surface
in CB



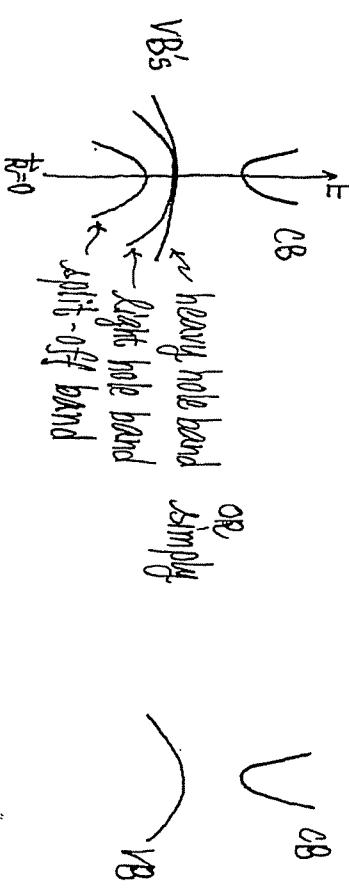
Germanium



direct gap



Physics is governed by the band structure around $k=0$ (E_F).
In studying semiconductor physics, the model band structure is: (near $k=0$)



Key physics has to do with some electrons near bottom of CB and some missing electrons near top of VB.

Tight-binding viewpoint:

Each atom: one s-orbital + three p-orbitals

4 atomic orbitals/atom
AND 4 electrons (e.g. $3s^2 3p^2$ ($1g_i$))

Two atoms per primitive cell

8 atomic orbitals per primitive cell

tight-bind to form 8 bands

\Downarrow
2N states/band \times 8 bands
= 16 N states

Total # electrons = $4 \cdot 2 \cdot N$ \leftarrow # cells per atom \leftarrow 2 atoms/cell

8N electrons completely fill 4 bands

8 bands \rightarrow 4 bands empty
 \rightarrow 4 bands filled \downarrow gap

D. Concept of Holes⁺ (useful in semiconductors)

T=0

empty CB

T \neq 0

some electrons in CB

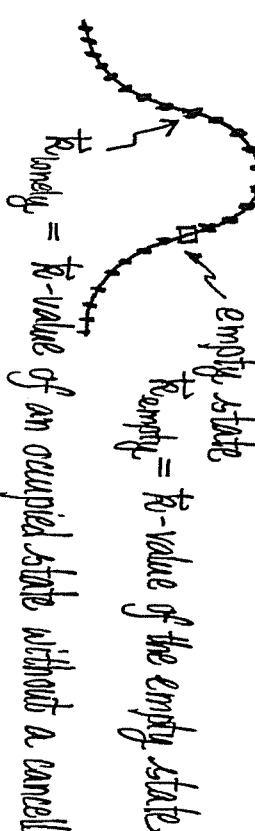
Semiconductors

full VBS

full band

empty states in otherwise full band

- Motivated to consider the behavior of a nearly filled band with a few empty states.
- We are interested in filled band with one empty state.



• System: Many electrons

- Behavior of "hole": results of a large number of electrons!

"Hole":
NOT simply the empty state
NOT simply the unoccupied state

+ Kittel, Ch. 8

(i) Consider the total crystal momentum of the electrons.

$$\begin{aligned}
 \sum_{\text{occupied states } k'} \hat{p}_{k' h} &= \sum_{\substack{\text{occupied states } k' \\ \text{except lonely}}} \hat{p}_{k' h} + \hat{p}_{k' \text{lonely}} = \hat{p}_{k' \text{lonely}} \\
 &= \sum_{\substack{\text{occupied states } k' \\ \text{except lonely}}} \hat{p}_{k' h} + \hat{p}_{k' \text{empty}} - \hat{p}_{k' \text{empty}} \\
 &= \sum_{\substack{\text{all states } k' \\ \text{except lonely}}} \hat{p}_{k' h} - \hat{p}_{k' \text{empty}} = -\hat{p}_{k' \text{empty}} \\
 &\Rightarrow \hat{p}_{k' \text{empty}} \text{ also shifts in } -\hat{x} \text{ direction}
 \end{aligned}$$

(ii) What is the semiclassical equation of motion $\frac{d}{dt}(\hat{p}_{k' h}) = ?$
 Under the influence of a uniform electric field \vec{E} ?
Physically, the force $-e\vec{E}$ acts on the electrons (occupied state)
 \Rightarrow shift in \vec{k} -values of the occupied states
 in $-\hat{x}$ -direction (left)

$$\begin{aligned}
 &\Rightarrow \hat{p}_{k' \text{empty}} = \hat{p}_{k' h} \text{ shifts in } +\hat{x} \text{ direction} \\
 &\text{i.e. the new particle (the hole) satisfies} \\
 &\quad \boxed{\frac{d}{dt}(\hat{p}_{k' h}) = +e\vec{E}} \quad (2)
 \end{aligned}$$

(see figure
on next page)

Regarding $e\vec{E}$ as the electric force on a hole,
 the hole behaves as if it is a particle
 with charge $+e$

$$\therefore \boxed{e_h = +e} \quad (3)$$

But the result looks simple!

It looks as if the contribution comes from one new particle, that we call a hole, with crystal momentum $\hat{p}_{k' h}$.

$$\boxed{\hat{p}_{k' h} = -\hat{p}_{k' \text{empty}}} \quad (1)$$

crystal momentum 'negative of crystal momentum of empty state of hole'

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Nearly Full band with one empty state

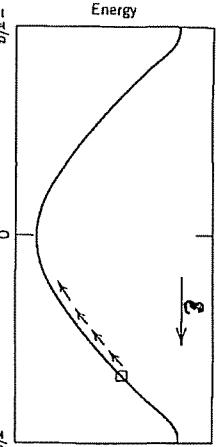
Electron dynamics:

It is the electrons that drift

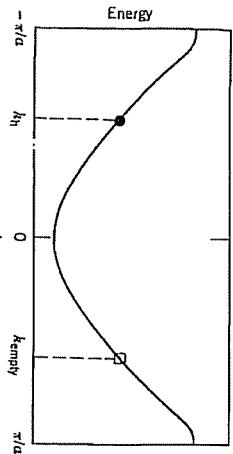
effectively, the empty state

moves in the

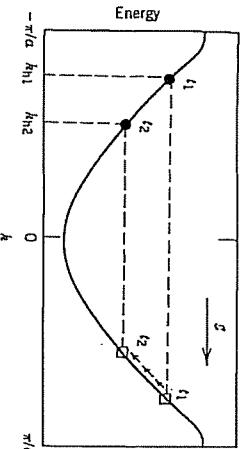
direction of the arrows



(a)



(b)



(c)

An electron energy band for a one-dimensional crystal. The square marks a state that is initially empty in an otherwise filled band. (a) When an electric field is turned on in the direction shown, the states indicated by arrows successively become empty as electrons make transitions to the left. (b) The band is completely filled except for the state marked by the square. Except for the electron in the state marked by a circle, each electron can be paired with another so the sum of their crystal momenta vanishes. The total crystal momentum for the band and the crystal momentum of the hole are both $\hbar \vec{k}_h$. (c) The empty state and unpaired electron for two times $t_2 > t_1$ when an electric field is in the direction shown. The change in \vec{k}_h is in the direction of the field.

$$\vec{J}_e = \sum_{\text{occupied states } \vec{k}} (-e) \vec{V}(\vec{k})$$

velocity of an electron in Bloch state \vec{k}

due to electrons

$$\vec{J}_e = -e \vec{V}(\vec{k}_{empty})$$

$$= -e \vec{V}(-\vec{k}_{empty})$$

$$= (-e) (-\vec{V}(\vec{k}_{empty}))$$

using $\vec{k}_{empty} = -\vec{k}_{empty}$

$$= +e \vec{V}(\vec{k}_{empty})$$

still electron viewpoint

$$\vec{J}_e = +e \vec{V}^0(\vec{k}_{empty}) - (-e) \vec{V}(\vec{k}_{empty})$$

$\vec{V}(\vec{k}_{empty})$ is velocity of Bloch state with $\vec{k} = \vec{k}_{empty}$

OR

$$\vec{J}_e = \sum_{\text{full band}} (-e) \vec{V}^0(\vec{k}) - (+e) \vec{V}(\vec{k}_{empty})$$

full band (all $\vec{k} \neq \vec{k}_{empty}$)

$$= +e \vec{V}(\vec{k}_{empty})$$

due to hole

Switch to hole picture: While $\vec{J}_h = \vec{J}_e = +e \vec{V}(\vec{k}_{empty})$

$$\equiv C_h \vec{V}_h(\vec{k}_h)$$

$$\therefore \vec{V}_h(\vec{k}_h) = \vec{V}(\vec{k}_{empty}) = \frac{1}{h} \vec{V}_k(\vec{k}) E(\vec{k}) \quad (4) \quad (\vec{k} = \vec{k}_{empty})$$

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(iii) Consider total electric current \vec{J} for a band with one empty state

contributions due to occupied states (electrons)

contributions due to unoccupied states (holes)

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$$\vec{V}_h(\vec{k}_h) = \vec{V}(\vec{k}_{\text{empty}}) = \frac{1}{\hbar} \vec{V}_t E(\vec{k})$$

hole picture

band of electronic states

One can also write $\vec{V}_h(\vec{k}_h)$ entirely in the hole picture

Recall: $\vec{t}_h = -\vec{t}_{\text{empty}}$

One can also write $\vec{V}_h(\vec{k}_h)$ entirely in the hole picture

$$\vec{V}_h(\vec{k}_h) = \frac{1}{\hbar} \vec{V}_{-\vec{k}_h} E(-\vec{k}_h)$$

$$= \frac{1}{\hbar} \vec{V}_{-\vec{k}_h} E(\vec{k}_h)$$

$$= -\frac{1}{\hbar} \vec{V}_{\vec{k}_h} E(\vec{k}_h)$$

$$= -\frac{1}{\hbar} \vec{V}_{\vec{k}_h} (-E(\vec{k}_h))$$

rewrite

Switch to hole picture

hole dispersion $E_{\text{hole}}(\vec{k}_h)$ is the electronic energy band

Write as:

$$\vec{V}_h(\vec{k}_h) = \frac{1}{\hbar} \vec{V}_{\vec{k}_h} E_{\text{hole}}(\vec{k}_h)$$

in analogy to $\vec{V}(\vec{k}) = \frac{1}{\hbar} \vec{V}_t E(\vec{k})$ for electrons

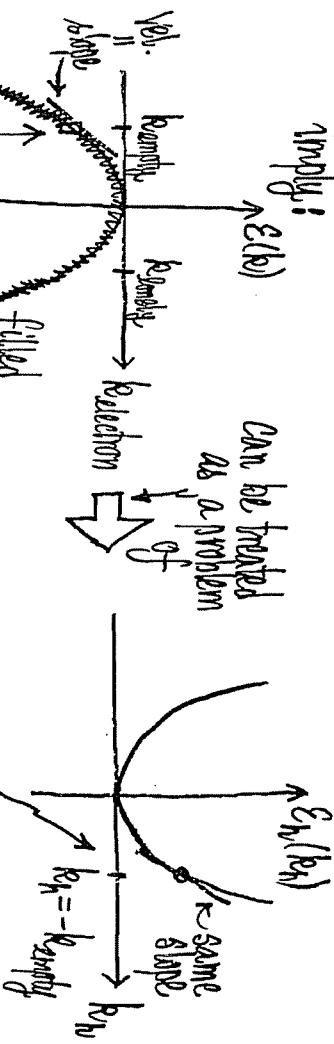
i. The hole behaves as if it has an energy dispersion relation (or hole energy band)

$$E_h(\vec{k}_h) = -E(\vec{k}_h) = -E(\vec{k}_{\text{empty}})$$

(5)

Sounds complicated! In pictorial form, properties (1), (4), (5) imply:

Can be treated as a problem of



One hole in an otherwise full band

One hole in an otherwise empty hole band

One empty state in otherwise full band

treat many electrons \rightarrow give same physical results! (+e charge)

treat one hole

effective mass tensor of a hole is the negative of the elements in the reciprocal effective mass tensor of an electron corresponding to the empty state.

(iv) It follows that (from figures above) the reciprocal effective mass tensor of a hole is the negative of the elements in the reciprocal effective mass tensor of an electron corresponding to the empty state.

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The reciprocal effective mass tensor of a hole is:

$$\left(\frac{1}{m_h^*}\right)_{ij} = -\frac{1}{\hbar^2} \frac{\partial^2 E(\vec{k})}{\partial k_i \partial k_j} \quad i, j = x, y, z \quad (6)$$

i.e., negative of the elements of the reciprocal effective mass tensor for the empty state.

Summary

A missing electron in a state to behaves as:

- charge +e , crystal momentum $\hbar \vec{k}_h = -\hbar \vec{k}$

$$V_h(\vec{k}) = \frac{1}{\hbar} \nabla_{\vec{k}} E(\vec{k}), \quad \left(\frac{1}{m_h^*}\right)_{ij} = -\frac{1}{\hbar^2} \frac{\partial^2 E(\vec{k})}{\partial k_i \partial k_j}$$

Notes⁺

Refs: Kittel Ch.8, Christian Ch.9

- charge enters when one needs to write down $\vec{F}_{\text{on hole}}$

• $\hbar \vec{k}_h$ enters into the semi-classical equation of motion

• Eq. of motion and $V_h(\vec{k})$ give: how \vec{k}_h changes due to $\vec{F}_{\text{on hole}}$ and then how \vec{k}_h changes (i.e. acceleration)

- Alternatively, one can invoke the effective mass m_h^* to relate acceleration and $\vec{F}_{\text{on hole}}$.

⁺These points are also valid in considering electron dynamics.

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E. The Chemical Potential μ of a Semiconductor

Semiconductor: $T=0 \nearrow$ empty CB



(Intrinsic semiconductor, no doping)

Result:

$$\mu(T) = \frac{E_c + E_v}{2} + \frac{3}{4} kT \ln\left(\frac{m_h^*}{m_e^*}\right)$$

(key result)

$$\underset{\text{At } T=0}{\mu(0)} = E_F = \frac{E_c + E_v}{2} = \frac{E_g + E_v + E_x}{2} = E_v + \frac{1}{2} E_g$$

$\Rightarrow E_F$ is in middle of the gap.

$$E_C = \text{energy of top of CB}$$

$$E_F = \text{gap}$$

$$E_V = \text{top of VB}$$

$$E_B = \text{bottom of VB}$$

• Recall: Background knowledge



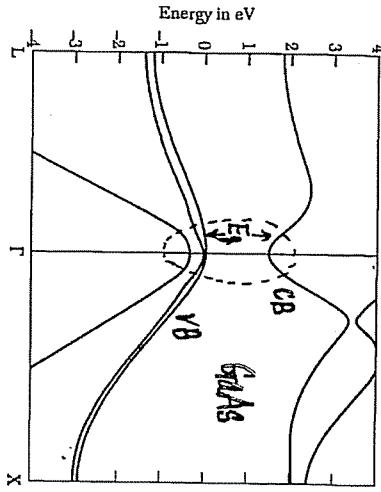
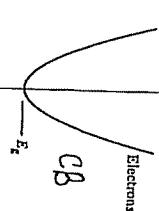
Band Structure of semiconductors could be complicated!

$$g(E) = \frac{V}{2\pi^2} \left(\frac{2m^*}{\hbar^2} \right)^{1/2} \sqrt{E}$$

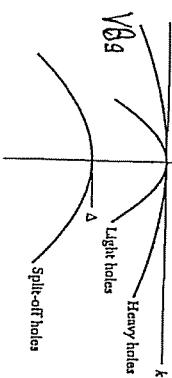
$$= 4\pi V (2m^*)^{1/2} \frac{\hbar}{\hbar} \sqrt{E}$$

with m^* describing the curvature.

Model semiconductor bands



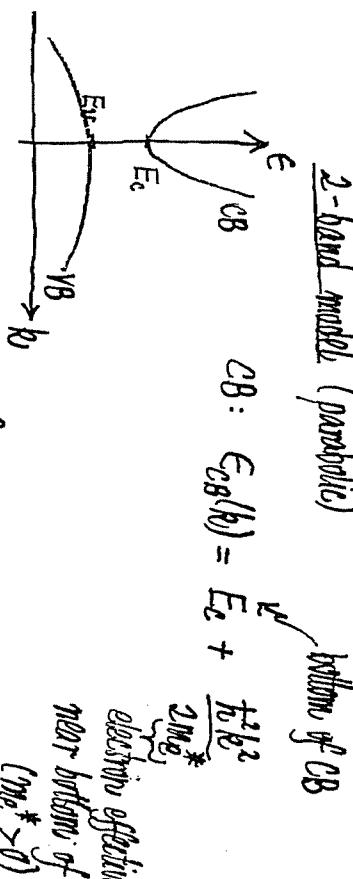
Direct gap, $E_g = \text{Band gap}$



Near band gap

For our purpose:

2-band model (parabolic)



V_B :

$$E_V(k) = E_V - \frac{\hbar^2 k^2}{2m^*_h}$$

or band gap

$(m_h^* = -m_e^* > 0)$

Crystal	Gap	$\frac{E_g, \text{eV}}{0 \text{K} - 300 \text{K}}$	Crystal	Gap	$\frac{E_g, \text{eV}}{0 \text{K} - 300 \text{K}}$
Diamond	i	5.4	SiC(hex)	i	3.0
Si	i	1.17	Tc	d	0.33
Ge	i	0.744	HgTe*	d	-0.30
α -Sn	d	0.00	PbS	d	0.286
InSb	d	0.23	PbSe	i	0.185
InAs	d	0.43	PbTe	i	0.190
InP	d	1.42	GaS	d	2.582
CaP	i	2.32	CdSe	d	1.840
CaAs	d	1.52	GaTe	d	1.607
GaSb	d	0.81	SnTe	d	1.14
AlSb	i	1.65	Cu ₁ O	d	0.3
					2.172
					-

$i = \text{indirect gap}$

$d = \text{direct gap}$

Crystal	Electron m_e/m	Heavy hole m_h/m	Light hole m_l/m	Split-off hole m_{so}/m	Spin-orbit Δ, eV
InSb	0.015	0.39	0.021	(0.11)	0.82
InAs	0.026	0.41	0.025	0.08	0.43
InP	0.073	0.4	(0.078)	(0.15)	0.11
CaSb	0.047	0.3	0.05	(0.14)	0.80
GaAs	0.066	0.5	0.082	0.34	0.34
Cu ₂ O	0.99	-	0.58	0.69	0.13

m_e^* and m_h^*
can be measured
by cyclotron resonance
measurements

Q: Given temperature T , can we calculate the number of electrons in CB (n_e) and the number of holes in VB (μ_h) per unit volume?

Key points to note:

Typically, $E_F \sim 1\text{ eV}$, $kT \sim 40\text{ eV}$ (room temperature). Anticipating that μ is somewhere in the middle of the gap, we have $E_C - \mu \sim \text{eV}$; $\mu - E_V \sim \text{eV}$

$$\Rightarrow \frac{E - \mu}{kT} \gg 1 ; \quad \frac{\mu - E}{kT} \gg 1$$

for E in CB

for E in VB

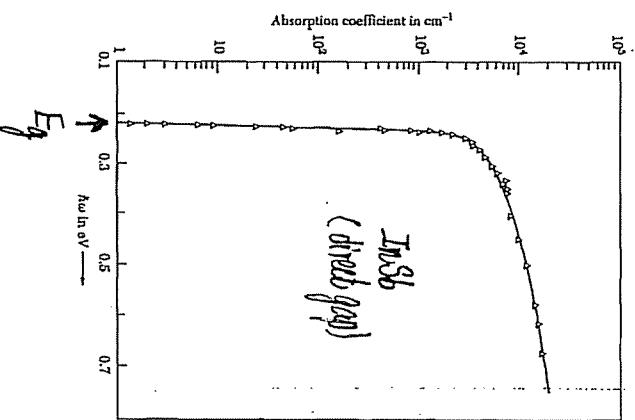
$$F(E) \approx e^{-(E-\mu)/kT} \ll 1 ; \quad F(E) \approx 1 - e^{-\mu - E/kT} \approx 1$$

Ψ
states in CB
have a tiny chance
of being occupied

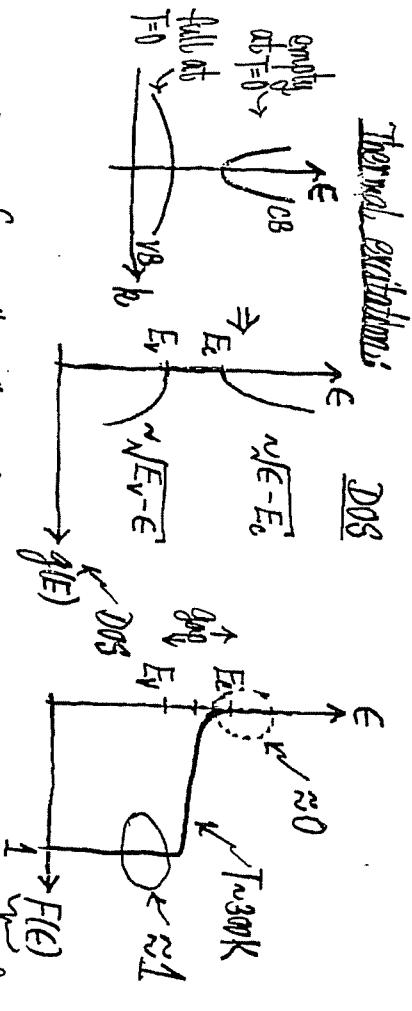
Ψ
states in VB
have a tiny chance
of being unoccupied

Q: What is $\mu(T)$ and $\lim_{T \rightarrow 0} \mu(T) = E_F$?

$T \neq 0$: $\left\{ \begin{array}{l} \text{some thermally excited electrons in CB} \\ \text{near bottom of CB} \\ \text{some missing electrons (holes) in VB} \\ \text{near top of VB} \end{array} \right.$



E_F can be measured by absorption experiments (room temperature)



2-band model

At $T=0$, all electrons are in VB and CB is empty.
 $N_c = \text{total number of electrons in the full valence band}$

$$= \int_{E_V}^{E_V} g_{VB}(e) de$$

$\curvearrowleft \text{ DOS of VB}$

At $T \neq 0$, some electrons are thermally excited to CB

$N_c = \text{number of electrons in CB}$

$$= \int_{E_C}^{E_F} g_{CB}(e) \frac{1}{e^{\beta(e-\mu)} + 1} de$$

$$g_{CB}(e) = \text{DOS of CB}$$

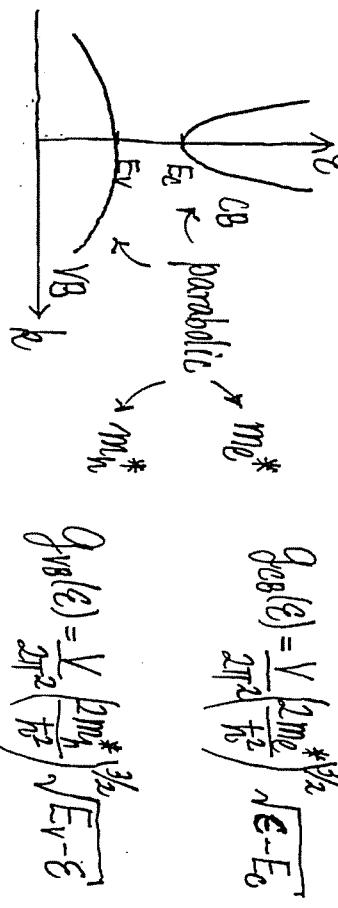
$$\approx \int_{E_C}^{E_F} g_{CB}(e) e^{-\beta(e-\mu)} de$$

$$\approx \int_{E_C}^{\infty} g_{CB}(e) e^{-\beta(e-\mu)} de$$

- extend upper limit to $+\infty$
- exponential tail \Rightarrow negligible error

Q: What is $\mu(T)$?

Yet to be determined!



$\therefore \frac{N_c}{V} = N_c = \text{electron number density (concentration) in CB}$

$$= \frac{1}{2\pi^2} \left(\frac{2m_e^*}{\hbar^2} \right)^{3/2} \int_{E_C}^{\infty} \sqrt{e - E_C} e^{-\beta(e-\mu)} de$$

$$= \frac{1}{2\pi^2} \left(\frac{2m_e^* kT}{\hbar^2} \right)^{3/2} e^{-\beta(E_C-\mu)} \int_0^{\infty} \sqrt{x} e^{-x} dx$$

$x = \beta(e - E_C)$

$$\Rightarrow N_c(T) = 2 \left(\frac{m_e^* kT}{2\pi \hbar^2} \right)^{3/2} e^{-\beta(E_C-\mu)/kT} = N_c^* e^{-\beta(E_C-\mu)/kT}$$

only a small electron concentration in CB

at $T \neq 0$

This is why doping with impurities, instead of thermal excitations, is used to introduce more electrons in CB.

Similarly, $n_V = \text{Electron concentration in VB}$ (it is nearly full)

$$= \frac{1}{V} \int_{E_B}^{E_V} g_{VB}(e) \frac{1}{e^{\beta(e-\mu)} + 1} de$$

$$= \frac{1}{V} \int_{E_B}^{E_V} g_{VB}(e) de - \frac{1}{V} \int_{E_B}^{E_V} \underbrace{\frac{g_{VB}(e)}{e^{\beta(\mu-e)} + 1}}_{\substack{\text{all states in VB} \\ (\text{full at } T=0)}} de$$

 N_e

$$\Rightarrow n_V = \frac{N_e}{V} - \frac{1}{V} \int_{E_B}^{E_V} \frac{g_{VB}(e)}{e^{\beta(\mu-e)} + 1} de$$

\uparrow
electron
number density
in VB

\uparrow
electron
number density
in VB

\uparrow
number density of Missing electrons
(in VB)

$\therefore p_V = \frac{1}{V} \int_{E_B}^{E_V} \frac{g_{VB}(e)}{e^{\beta(\mu-e)} + 1} de$

\downarrow
call it $p_V = \text{hole concentration}$
in VB

$$\approx \frac{1}{V} \int_{E_B}^{E_V} \frac{1}{e^{-\beta(\mu-e)} + 1} g_{VB}(e) de = 2 \left(\frac{m_h^* kT}{2\pi\hbar^2} \right)^{3/2} e^{\beta(E_V-\mu)}$$

$$\Rightarrow p_V(T) = n_V^* \cdot e^{\beta(E_V-\mu)} = n_V^* \cdot e^{-\beta(\mu-E_V)}$$

$$n_V^* \equiv \left(\frac{m_h^* kT}{2\pi\hbar^2} \right)^{3/2}$$

Key results:

$$n_e(T) = 2 \left(\frac{m_e^* kT}{2\pi\hbar^2} \right)^{3/2} e^{-(E_V-\mu)/kT}$$

$$p_V(T) = 2 \left(\frac{m_h^* kT}{2\pi\hbar^2} \right)^{3/2} e^{-(E_V-\mu)/kT}$$

- These equations are valid for intrinsic (pure) and extrinsic (doped) semiconductors.
- $\mu(T)$ is yet-to-be-determined.

$$n_e \cdot p_V = 4 \left(\frac{kT}{2\pi\hbar^2} \right)^3 (m_e^* m_h^*)^{3/2} e^{-E_g/kT} = n_e^2 = n_{\text{intrinsic}}^2$$

\downarrow
depends on E_g only, independent of μ
valid for pure and doped semiconductors.

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E_F and $\mu(T)$ for intrinsic (pure) semiconductors

(i) Intrinsic (pure) semiconductors

$$n_e = \rho_V \quad \begin{matrix} \text{electrons in CB must come} \\ \text{from missing ones in VB} \end{matrix}$$

this equality fixes $\mu(T)$

$$2 \left(\frac{m_e^* k T}{2\pi \hbar^2} \right)^{3/2} e^{-(E_F - \mu)/kT} = 2 \left(\frac{m_h^* k T}{2\pi \hbar^2} \right)^{3/2} e^{(E_V - \mu)/kT}$$

Solve for $\mu(T)$:

$$\mu(T) = \underbrace{\frac{E_C + E_V}{2}}_{\text{'mid-gap'}} + \frac{3}{4} kT \ln \left(\frac{m_h^*}{m_e^*} \right)$$

(ii) At $T=0$,

$$E_F = \lim_{T \rightarrow 0} \mu(T) = \frac{E_C + E_V}{2} = \frac{E_C - E_V + 2E_V}{2}$$

$$= E_V + \frac{E_C}{2}$$

E_F is at mid-gap

+ The intrinsic regime is where thermal excitations from VB to CB dominate. Thus, doped semiconductors at sufficiently high temperatures also satisfy the intrinsic regime.

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(iii) $T \neq 0$, since $m_e^* < m_h^*$

$$\ln \frac{m_h^*}{m_e^*} > 0$$

$$\Rightarrow \mu(T) = E_V + \frac{E_C}{2} + \underbrace{\frac{3}{4} kT \ln \left(\frac{m_h^*}{m_e^*} \right)}_{> 0}$$

In intrinsic semiconductors, $\mu(T)$ shifts towards bottom of CB (i.e., up from mid-gap). (Why?)

(iv) Given E_g , m_e^* , m_h^* , T :

$$n_e = \rho_V = 2 \left(\frac{kT}{2\pi \hbar^2} \right)^{3/2} (m_e^* m_h^*)^{1/4} e^{-E_g/2kT}$$

$$\text{Recall: } \sigma = \frac{n e^2 r}{m} \quad (\text{actually both electrons and})$$

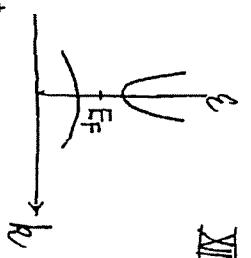
$$\log \sigma = \log f(T) - \frac{E_g}{2k_B T} \quad \begin{matrix} \text{folds contribute} \\ \text{down} \end{matrix}$$

(v) Estimate:

$$m_e^* = m_h^* = m_e \quad (\text{not true})$$

$$E_g \approx 1 \text{ eV}, \quad T = 300 \text{ K}$$

$$n_e = \rho_V \sim 10^{15} \text{ cm}^{-3} \sim 10^{21} \text{ m}^{-3} \quad (\text{metals: } 10^{28} \text{ m}^{-3})$$



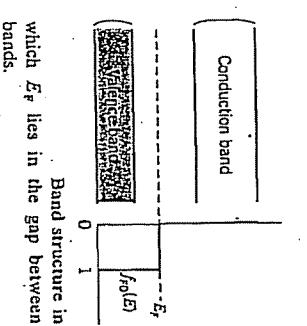
III(5)

$E_g \cdot E_g \approx 1\text{eV}$

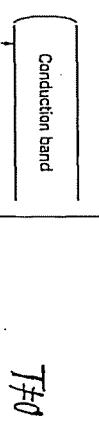
(V) Why does a difference of 2-3 eV in E_g change a material from semiconductor to insulator?

Ans: Since E_F is near mid-gap, what matters is the tail of the Fermi-Direc distribution!

$T=0$

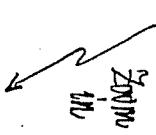
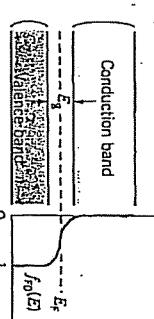


Band structure in which E_F lies in the gap between bands.



When $E_g \gg kT$, the conduction band is still unpopulated. This situation is characteristic of an insulator.

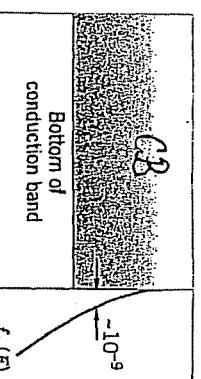
a semiconductor. The gap is much smaller than in an insulator, so there is now a small population of the conduction band.



(Still has about 10^{10} electrons in CB in cm^3)

$T \neq 0$ semiconductor

$\frac{10^{-9}}{\text{cm}^3}$



The tail of the Fermi-Dirac distribution function near the bottom of the conduction band. On the scale of this diagram, the "1" of $f_{FD}(E)$ is 1000 km off to the right and E_F is about 1 m below the bottom of the page.

E_g is so large that basically there is no electron in CB at room temperature

e.g. $E_g \approx 5\text{eV}$ (insulator)

$T=300\text{K}$

$$e^{-E_g/kT} \approx 10^{-44}$$

No electrons in CB

The Fermi-Dirac distribution function near the top of the valence band, showing the small fraction of empty states.

($1 - 10^{-9}$) prob. of being unoccupied

$$\left. \begin{array}{l} E_g \sim 1\text{eV} \\ T=300\text{K} \end{array} \right\} e^{-E_g/kT} \approx 10^{-9}$$

Only 1 electron out of 10^9 contributes to conduction

[Silicon at room temperature, about 10^{11} electrons/ cm^3 , i.e.

only about 1 electron out of 10^{10} contributes!]

[But, if $E_g \approx 5\text{eV}$, practically 10^9 electrons in CB.]

III(6)